# COLLOIDS IN AGRICULTURE

C. E. MARSHALL

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# COLLOIDS
# IN AGRICULTURE

BY

C. E. MARSHALL, M.Sc., Ph.D.
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*First Published in* 1935

Printed in Great Britain by
Butler & Tanner Ltd., Frome and London

# PREFACE

I have written this book with an eye to the needs of two classes of readers. Firstly, I hope it will prove useful to our county organizers, district lecturers and rural instructors—indeed, to all who are engaged in scientific agriculture and who are interested in the application of our latest knowledge to their field work and their teaching.

I have written also for our agricultural students. To them, few subjects are more confusing than colloid chemistry, due largely to our haphazard methods of teaching. The student is first introduced to the subject when silicic acid and its properties are under discussion. No sooner has he made a nodding acquaintance with its novel properties than the chemistry of the silicates claims his attention. Months later, he is plunged, without further preparation, into the study of colloids in soils. Here the discussion is on an elevated plane. Controversies and anomalies surround him on every side. Finally, in an introduction to the chemistry of the feeding-stuffs he encounters the proteins, whose colloidal properties, although again new to him, seem vague and soothing after the desperate feats of memory involved in learning the chemistry of the amino-acids.

My best thanks are due to the following: To my wife for her untiring help and encouragement in the preparation of the manuscript. To Professor J. McGregor, B.Sc., for his valuable suggestions after reading through the manuscript in the interests of the agriculturists. To Mr. I. M. Mackay, B.Sc., who very kindly undertook the drawings. To Dr. B. A. Keen and the Cambridge University Press for permission to use Fig. 10.

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# CONTENTS

## PART I

## THE REALM OF COLLOIDS

CHAP. PAGE

I The Nature of Colloids . . . . . 1

II The Formation of Colloids . . . . 8

The influence of solubility. The rate of formation of nuclei. The rate of growth of nuclei. Dispersion methods.

III The Properties of Small Particles in Suspension 17

The Brownian movement. Diffusion. Dialysis and ultrafiltration. Osmotic pressure. Coagulation. Settling under gravity. Optical properties.

IV The Properties of Molecules at Surfaces . 33

The influence of dissolved substances. The structure of capillary-active molecules. Absorption and adsorption. Molecules at the solid—liquid interface. Reactions of adsorbed molecules.

V Ions at Surfaces . . . . . . 42

Dissociation. Dissociation at an interface. The influence of ions in solution. Electrical properties and coagulation. Hydrophobe and hydrophile colloids. Reactions of surface ions. Mutual coagulation of colloids.

VI Sols and Gels . . . . . . . 59

The sol–gel transformation. The properties of hydrophile sols. Protective action. Water in gels. The winter hardiness of plants. Drought resistance.

## PART II

## COLLOIDS IN THE SOIL

CHAP. PAGE

VII THE MINERAL COLLOIDS OF SOIL . . . . 69

Mechanical composition. Colloidal minerals in soil. The hydrated oxides. The phosphates. The clay minerals. Base exchange. The colloidal properties of the clays. Clays as gels.

VIII THE ORGANIC COLLOIDS OF SOIL . . . . 101

The complex nature of humus. The colloidal properties of humic matter.

IX COLLOIDS IN SOIL FORMATION PROCESSES . . 111

Soil development under arid conditions. Soil development under semi-arid conditions. Soil development under humid conditions. Podsol formation.

X COLLOIDS AND SOIL TEXTURE . . . . 123

Soil colloids and cultivation. The dynamometer. " Single value " soil constants. Moisture relationships. Seasonal variations in physical conditions. The influence of fertilizers on soil texture. Crumb formation.

## PART III

## COLLOIDS IN PLANT AND ANIMAL LIFE

XI SOME COLLOIDAL MATERIALS PRESENT IN LIVING ORGANISMS . . . . . . . 135

Colloidal carbohydrates ; starch, lichenin, glycogen, cellulose, lignocellulose. Proteins.

XII COLLOIDAL ARCHITECTURE IN BIOLOGICAL STRUCTURES 150

The structure of gels. The structure of natural fibres ; cellulose, the fibrous proteins.

XIII MILK AND MILK PRODUCTS AS COLLOIDAL SYSTEMS . 160

The butter fat emulsion. The casein sol. Other colloids of milk. Butter and butter making. Cheese and cheese making.

XIV SMOKE DAMAGE AND PLANT PROTECTION . . 171

Smoke damage. Plant protection.

INDEX . . . . . . . . . 179

# COLLOIDS IN AGRICULTURE

## PART I

## *THE REALM OF COLLOIDS*

## CHAPTER I

## THE NATURE OF COLLOIDS

The student of agriculture who is perforce to some extent a student of chemistry is well aware of the differences in chemical and physical properties between solid substances and their solutions in liquids such as water. These differences may be summed up very simply. In the crystalline solid the molecules (or ions) are held firmly together and are arranged in a definite geometrical pattern. In the solution they are quite independent of one another and are in continual irregular motion. If, however, the solid and the solution are considered when they are in actual contact with one another, it will readily be seen that a third type of molecule is present. At the surface of the solid the molecules are rigidly held only by similar units surrounding them in the surface and behind it. In front they are exposed to continual attraction and bombardment by molecules of the solvent. It is to be expected therefore, that these surface molecules will have properties to some extent intermediate between those of the solid and those in the liquid, showing a chemical reactivity akin to that of the true solution and a rigidity of the same order as that in the interior of the solid. Besides these surface molecules of the solid, the liquid molecules at or near the solid surface are in an environment very different from those which are completely surrounded only by other molecules of the liquid. The unbalanced chemical forces of the surface molecules can attract and hold a layer of liquid molecules very firmly. These bound molecules will have lost a large part of their former mobility and will behave rather as molecules of a solid than those of a liquid. They may also be much more closely packed together than their more mobile fellows, for these latter have actually considerable free space in which to execute their motion.

Now the type of surface we have been considering which involves some modification in the properties of two kinds of molecules is known as an *interface.* Colloid chemistry in the broad sense may be briefly described as the chemistry of interfaces, that is, the chemistry of molecules whose normal properties are modified by their presence at a surface. In making the definition we need not restrict ourselves to the very simple case described above. In the first place, several kinds of molecules may be and usually are concerned at the same time. A quartz pebble in the sea will have at its surface not only these interfacial molecules of quartz and of water, but each of the dissolved constituents of sea-water as well, and the properties of these too will differ from those of their fellows in the body of the liquid. Nor is it necessary to consider only the solid-liquid interface. We find similar effects with gas-liquid, gas-solid, liquid-liquid and to a smaller extent with solid-solid interfaces. The study of interfaces thus extends over the whole realm of chemical substances, but in practice it is likely to be limited to those which exhibit so extensive a surface that the molecules with modified properties form an appreciable proportion of the total number present.

It should be noted at this point, that although colloid chemistry has been defined as the study of interfaces, the two terms colloid and interface are not exactly synonymous. The reasons for the divergence in meaning are historical. Between these two words lies the whole story of the triumphs and controversies of this new branch of science as one traces it from Thomas Graham down to the present day. There is no space to say more about it here; nevertheless, the query of the puzzled agriculturist, " What is a colloid ? ", must be answered.

The colloid chemist, as we have seen, is interested in all systems in which the peculiar properties of surface molecules are detectable. A moment's consideration will show that he can only detect these peculiarities chemically when the surface is comparatively large. He can estimate quantities down to one milligram with reasonable accuracy using a good analytical balance. Knowing that 1 cubic centimetre of water contains $3{\cdot}37 \times 10^{22}$ molecules, one can readily calculate the area of the water surface which contains 1 milligram of surface water molecules. It is about 30,000 sq. cm., an area which is much too large for convenient handling when exposed as a single surface. Let us see how such a surface area can be obtained in a form more suitable for manipulation.

We commence with a cube of material whose side is 1 cm. long. The total surface of the cube is 6 sq. cm. The surface exposed may be increased in several ways (see Fig. 1):

(*a*) By cutting into thin sheets. In Fig. 1 (*a*) there are 10 such sheets and the total surface exposed is 20 sq. cm. (there are now 20 surfaces of 1 sq. cm. each) + 4 sq. cm. (the edges of the sheets being 4 faces of the original cube) = 24 sq. cm. With thinner sheets the surface is naturally greater. 10,000 sheets would give 20,000 + 4 = 20,004 sq. cm., each sheet being only $\frac{1}{10000}$ cm. in thickness.

(*b*) By further subdivision of the sheets into rods of square cross-section. In Fig. 1 (*b*) there are 100 such rods and the total surface exposed is $(100 \times \frac{4}{10}) + 2 =$ 42 sq. cm. Again, we may diminish the thickness, this time both ways, keeping the length of the rods 1 cm. and so increase the surface. Taking 1,000,000 rods of $\frac{1}{1000}$ cm. thickness the total surface would be $(1{,}000{,}000 \times \frac{4}{1000}) + 2 = 4002$ sq. cm. Multiplying the number by 100 and diminishing the thickness to $\frac{1}{10000}$ cm. gives a surface of 40,002 sq. cm.

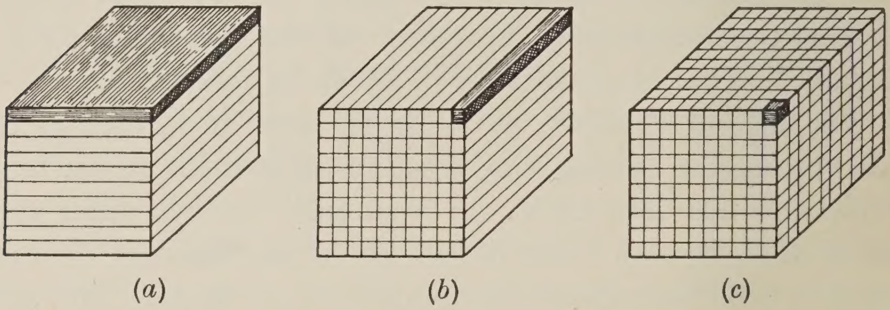

FIG. 1.—The three ways of increasing the total surface of a cube.

(*c*) The rods can be subdivided into small cubes. In Fig. 1 (*c*) 1000 small cubes are produced in this way. The total surface is $1000 \times \frac{6}{100} = 60$ sq. cm. If now the subdivision is carried further so that each small cube has a length of $\frac{1}{10000}$ cm. then the total surface will be $(10{,}000)^3 \times \frac{6}{(10000)^2} = 60{,}000$ sq. cm.

From this simple example a number of important conclusions follow. Firstly, the total surface is proportional to the degree of subdivision. A very large surface may thus be exposed by a small quantity of substance, provided the degree of subdivision is sufficiently great. In the example just considered a degree of subdivision of 10,000 per cm. gives surfaces of 20,000, 40,000 and 60,000 sq. cm. for plates, rods and cubes respectively. These surfaces are of the right order of magnitude for the properties of the surface molecules to be detected chemically; since the figure we arbitrarily chose to suit the chemist's convenience was 30,000 sq. cm., corresponding to 1 milligram of surface water molecules.

Secondly, it can be seen from the figures given, that on comparing plates, rods and cubes at the same degree of subdivision the ratio of the surfaces is 1 : 2 : 3, provided always that the thickness of the plates or rods is small compared with the length.

Having shown that a sufficiently large surface can be produced by subdivision, it might be thought that the chemist could now proceed to define a colloid by saying that all systems having one or more constituents at a degree of subdivision of 10,000 per cm. or over (true solutions being excepted) are colloidal systems. This definition has indeed been adopted by many who are particularly interested in soils, whereas most of those who have concerned themselves with the general properties of colloids have used a figure of 50,000 or even 100,000 per cm. for the necessary degree of subdivision. (In the parlance of colloid chemistry the term "*degree of dispersion*" is used instead of degree of subdivision. The term implies that one substance, known as the "*disperse phase*" is disseminated or dispersed throughout the other, known as the "*continuous phase*" or the "*dispersion medium.*") This choice has, indeed, some advantages. At this higher degree of dispersion the special characteristics of the surface molecules are easily observed, even in a small quantity of material. Further, it happens that $\frac{1}{50000}$th of a centimetre (or 0·0002 mm.) represents roughly the limit beyond which the best modern microscope will yield no further information of structural form. The nature of light itself sets a limit to the power of the microscope as an instrument for observing fine detail. It is true that particles less than 0·2 $\mu$[1] can be observed under suitable conditions, but the image obtained no longer gives a true indication of their shape.

Particles less than 0·2 $\mu$ or 200 m$\mu$ are termed *submicrons.* In this book we shall not restrict ourselves to the study of submicrons. We shall include not only the larger units up to 1 $\mu$ in diameter but also those interesting structures which are built up of submicrons in orderly arrangement and which enable all living things to achieve strength and rigidity with so marvellous an economy of material.

We have now briefly surveyed the field and may make our definition. We can say simply that a colloid is a substance in so fine a state of subdivision that its particles are (in one dimension at least) less than 1 $\mu$ (or less than 0·2 $\mu$ if we prefer to make the microscope our judge). However, although this definition has been widely used it is open to a serious objection. As we have seen, the study of colloids involves at least two kinds of molecules; so that it is better to avoid the term colloidal substance which implies only one, and to think, rather, of colloidal systems. A colloidal system may be defined as a system in which a large interface has been attained by the dispersion of one or more of the constituents into units not larger than 1 $\mu$ or 0·2 $\mu$ as the case may be. The units need not be independent of one another as they are in the case of suspensions of small particles in water. A sponge filled with water whose pores were only 0·2 $\mu$ in size would also be a colloidal system, and we shall come across some important examples of this kind amongst the jelly-like substances in nature.

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[1] The microscopist usually expresses length in terms of thousandths of a millimetre, this unit being termed a micron and written 1 $\mu$. The colloid chemist requires a still smaller unit and has adopted one-thousandth of a micron or one-millionth of a millimetre, written 1 m$\mu$, or less correctly 1 $\mu\mu$. Thus 1000 m$\mu$ = 1 $\mu$ and 1000 $\mu$ = 1 mm.

# CHAPTER II

# THE FORMATION OF COLLOIDS

Few contrasts are more striking than that which has so often been drawn between the practical methods of the chemist and those of plant or animal as each seeks to synthesize some complex organic compound. The disparity is no less great when the difficulty and even the very caprice of the preparation of colloidal systems in the laboratory is contrasted with the ease and certainty with which living matter forms and uses them. Nature, indeed, has so far solved these problems, with which the colloid chemist somewhat blindly grapples, that she can play, as it were, many subtle variations on a single theme. Thus the starch grains and the cellulose fibres of the plants, the milk casein and the blood fibrin of the animals, the chitinous shell of the insects, all these and many besides bear a stamp, sometimes almost imperceptible and sometimes unmistakable, of the natural laboratory in which they were prepared. It is, as yet, not possible to enumerate all the factors which are at work in the preparation of colloidal systems, but three of the most important are well recognized and must be discussed here.

**The Influence of Solubility.**—Substances, whether solid, liquid or gaseous, which can dissolve in liquids are usually regarded as having a constant solubility at a given temperature and pressure; that is, the maximum percentage of the dissolved substance in the solution is fixed and is independent of the relative amounts used. Thus a saturated solution of alum contains 15 grammes per 100 grammes of the solution at 20° C., whether it is in contact with one large crystal or with many small ones, or whether only a little or a large quantity of solid is actually present. We may deduce therefore, as a simple corollary to these facts, that the solubility is independent of the extent of the interface between the solid and the liquid, and the same is true also of gases and liquids. It is found, however, that substances in a very finely divided condition indeed, show an enhanced solubility, the increase becoming larger as the degree of subdivision increases. For instance, gypsum has a solubility of 0·227 per cent. at 20° for any size of particle down to 50 $\mu$, but for particles of 5 $\mu$ it is 0·229 per cent. and for those of 0·5 $\mu$, 0·248 per cent. As we have seen, this effect cannot be due simply to the increase in the surface exposed. It may be regarded as a property of the edge or corner molecules of small crystals, for it is easy to see from Fig. 1 in the previous chapter that the ratio between these and the number of purely surface molecules is bound to increase with the degree of subdivision. The effect is also found with small spherical droplets of a liquid suspended in another liquid, and in this case a simple mathematical formula connects the radius with the solubility. In general, therefore, solubility increases with the curvature of the surface, and the curvature naturally becomes greater as the particle size decreases.

Let us take a concrete example as an illustration of the importance of this effect in the preparation of colloidal systems. Gypsum can readily be produced by the interaction of calcium chloride and sodium sulphate.

Suppose the two solutions to be mixed in equivalent amounts and in such concentrations that the final solution would be expected to contain 0·248 per cent. gypsum. The chemist would regard this as a *supersaturated* solution because it contains more gypsum than corresponds to the ordinary solubility. He would therefore expect a precipitate to form containing all the gypsum over and above this amount (0·227 per cent.). But from what has been said above, it will be seen that the solution is only supersaturated with respect to particles larger than 0·5 $\mu$ ; for smaller particles it does not reach saturation, and any such particles if added to the liquid would dissolve. On the other hand, particles greater than 0·5 $\mu$ would rapidly grow in the liquid as the excess gypsum in solution crystallized out on them. Under the conditions we have postulated, therefore, it would be impossible to produce a precipitate of gypsum with particles less than 0·5 $\mu$, and each degree of supersaturation corresponds to a definite minimum size of particle, this minimum decreasing as the degree of supersaturation increases. Thus the first condition for the production of colloidal particles is the attainment of the required degree of supersaturation. Other things being equal the higher the degree of supersaturation at the moment of formation of the particular molecules concerned, the smaller will be the particles produced. In the case of readily soluble substances, no great degree of supersaturation can possibly be attained, so that it is impossible to produce colloidal particles whose molecules are readily soluble in the liquid. Further, in the formation of a colloid by such a method as we have considered, there are inevitable differences in actual particle size. Now the less soluble larger particles, under these circumstances, will be bound to grow at the expense of the more soluble smaller ones, the system becoming progressively coarser. This effect is very marked in systems which have a measurable solubility, but becomes small for insoluble substances. In this way we may explain the fact, well known to the analyst, that the substances which readily form stable colloidal systems are those which have immeasurably small solubilities in the particular liquids concerned.

The degree of supersaturation as we have seen, sets a limit to the size of the smallest possible stable particle, but the actual size produced under any given conditions depends on two other factors; the rate of formation of the smallest possible particles, or *nuclei* as they are called, and their rate of growth once they have been produced.

**The Rate of Formation of Nuclei.**—So little is known about the all-important process of the formation of nuclei that a long discussion of it here would be out of place. It is evident that in the production of nuclei, a number of molecules must have adhered to one another after collision. The chances of stable nuclei being formed will therefore be enhanced by increasing the number of collisions per second. There are two ways of doing this; one is to increase the concentration and the other to raise the temperature. It is certain, however, that only a small fraction of the total number of collisions actually leads to the formation of nuclei, and presumably the effective collisions are chiefly those occurring between the slowest of the molecules present. Such slow molecules have not sufficient energy to overcome the attractive forces holding them together when once they have come into contact. The conditions are somewhat similar to those which would be found in a game of snooker played with sticky balls. Now the average speed of molecules is increased by raising the temperature, so that one would expect the nucleus formation velocity to decrease, unless the increase in the total number of collisions more than counter-balanced the decrease in their effectiveness. In most cases, the nucleus formation velocity is diminished by rise of temperature.

The nucleus formation velocity is also affected in some way which is not yet understood, by the presence of other molecules in solution. Sometimes these have so pronounced an influence, even in minute concentrations, that the formation of nuclei is completely inhibited. Very few systems have been investigated from this point of view.

**The Rate of Growth of Nuclei.**—As soon as the nuclei have been formed they will begin to grow by crystallization since they are in a supersaturated solution. If the rate of nucleus formation is high and that of crystallization low, then we may expect the final particles to be small. In the contrary case they will be comparatively large. If both velocities are high or both are low, then systems will be obtained having many different sizes of particles, because while the nuclei first formed have been growing others have continually been produced.

Since crystallization is a somewhat similar process to nucleus formation it might be expected that the effect of increasing the concentration would also be to increase the speed of crystallization. This is found to be the case. Rise in temperature affects the system in three ways—it generally alters the degree of supersaturation, it increases the speed of the molecules and it also increases the number of collisions between them and the surface of the nuclei. The presence of other molecules in the solution often has a marked effect on the speed of crystallization. At the surface of a crystal, as we saw in the last chapter, the molecules are endowed with peculiar reactivity, in virtue of which they can attract and hold different molecules from the solution. Heavy molecules, particularly those of organic substances, are very strongly held in this way, and in consequence of their presence the rate of crystallization of the nuclei is much reduced. Further, since the different faces of crystals contain different arrangements of the constituent atoms and molecules, the magnitude of the effect will vary from one face to another, causing changes in their relative rates of growth. For this reason the presence of foreign molecules not only decreases the general speed of crystallization, but can also change the form of the crystals.

In the preceding discussion we have considered the formation of a small crystalline particle, but the order and the relative importance of the different stages are much the same for non-crystalline—(*amorphous*) particles, in which the constituent atoms or molecules are not arranged in such regular geometrical patterns as they are in the crystals.

When particles of colloidal size have been produced, a further process often occurs in which they grow by adhering to one another, following upon collisions. This process is usually termed coagulation and will be discussed later. Sometimes it occurs in a slow and regular manner like an ordinary crystallization, and this particular type is often referred to as the " ageing " of a colloidal system. It can go on for days or even for years, and may eventually lead to the production of particles too large to be described as colloidal.

The processes so far described in which colloidal systems are built up from molecules are usually termed condensation methods. They are more important in the laboratory and in nature than the dispersion methods which start from coarse material and break it down into particles of colloidal size. These latter, however, are much employed technically and are of some interest to the agriculturist because of their use in the preparation of insecticides and fungicides and in certain branches of dairying.

**Dispersion Methods.**—It can readily be imagined that the ordinary grinding methods, such as the use of the pestle and mortar in the laboratory, or the steel ball mill on the technical scale are not efficient in producing particles of solids less than 5 $\mu$ in diameter. In order to attain a greater degree of subdivision a number of machines known as *colloid mills* for dealing with solid particles and as *homogenizers* for dealing with liquid particles have been developed. Although there is some variation in detail the principle of all these machines is the same. The particles to be split up are forced between two hard smooth surfaces which can rapidly be rotated in opposite directions so that the individual particles are subjected to a large shearing force. (In some models only one surface rotates.) The distance between the two surfaces, which are often cone-shaped, is only a few $\mu$, so that solid material must already be finely ground before it can be used. Generally the suspension is forced in near the centre of rotation and escapes at the periphery of the cone. The efficiency of the machine depends very largely on the mechanical properties of the solid. Crystalline solids which have a ready cleavage are comparatively easily broken down, but even in the most favourable cases the amount of material less than 1 $\mu$ produced is small. The conditions are more favourable when liquids are to be subdivided into very small droplets—a process which is known as *emulsification*. In this case it is generally necessary to add a third (colloidal) substance to the two liquids so that as soon as the droplets have been produced they may immediately acquire a coating of this colloidal substance to prevent them from coalescing afterwards (for the general theory of the stability of colloidal systems see Chapter V). Thus a paraffin emulsion for use as an insecticide can readily be made by forcing a mixture of paraffin and soap solution through a homogenizer. In this case the soap forms the protective coating around the small droplets of paraffin. In absence of soap an emulsion of paraffin in water could certainly be prepared, but it would rapidly separate into two layers because the droplets of paraffin would unite whenever they collided with one another and would thus soon become large enough to rise quickly to the surface.

In one important instance, however, the addition of a protective colloid is unnecessary, because it is already present in the system. An interesting development in the dairying industry has been in the production of cream from butter and milk. Here the proteins present in the milk are effective in protecting the butter-fat particles from coalescence. One of the reasons why the process is used is that the homogenized product appears "richer" to the eye and to the palate than a natural cream of the same fat content. It is possible, therefore, to simulate natural cream with a homogenized cream having a lower butter-fat content. In the feeding of infants homogenized milk is found to be more easily digested than ordinary milk because of the smaller size of the fat globules, which then approximate closely to those of human milk.

### SUPPLEMENTARY READING

The theory underlying the preparation of colloidal systems is given very fully in H. Freundlich's *Kapillarchemie,* Vol. 1 (4th ed., Leipzig, 1930), of which there is also an English translation, *Capillary and Colloid Chemistry* (London, 1929). Practical details are given in E. Hatschek's *Practical Colloid Chemistry* (London, 1925) and R. N. Holmes's *Laboratory Manual of Colloid Chemistry* (2nd ed., New York, 1928). R. Clayton's book *Emulsions* (2nd ed., London, 1928) should be consulted for further particulars of the dispersion methods as applied to oils. R. Zsigmondy's *Kolloidchemie* (2 vols., 4th ed., Leipzig, 1925) combines many preparative details with a full theoretical discussion of colloids.

# CHAPTER III

# THE PROPERTIES OF SMALL PARTICLES IN SUSPENSION

Towards the end of Chapter I it was pointed out that colloidal systems are of two kinds—those in which the dispersed particles are independent of each other and those having a sponge-like or felt-like structure in which the dispersed units are held together. The former class are usually described as *sols*, the latter as *gels*. To the agriculturist both types are of importance and it is a matter for regret that the study of the gels has lagged so far behind that of the sols. The reason for the disparity lies largely in the fact that the sols have lent themselves to exact mathematical treatment and in a manner which has had a marked influence on general theory. The gels have proved more difficult both theoretically and experimentally.

In the present chapter we shall consider those physical properties of small particles in suspension which depend on size and number rather than on the peculiarities of the surface exposed.

**The Brownian Movement.**—Few observations made by biologists have had the same far-reaching consequences to chemical theory as that of R. Brown, a botanist, who in 1827 noticed that small grains of pollen suspended in water appeared under the microscope to be in ceaseless irregular motion. It was soon established beyond doubt that this property was possessed by all small particles in suspension and that the motion was not due to any external force, but was accounted for by the bombardment of the particles by the molecules of the liquid, which executed a similar but even more violent motion. This irregular molecular motion is most violent in gases and is practically absent from solids, the liquids occupying an intermediate position. The mathematical theory of this motion (known as the Kinetic Theory) does not concern us here, but since certain important properties of colloidal particles cannot be understood without some reference to it, we must discuss very simply three of the mathematicians' conclusions.

Let us consider not the actual speed of the particles, but their kinetic energy, which in the simplest case of a particle moving in a straight line is $\frac{1}{2} m v^2$, $m$ being the mass of the particle and $v$ its velocity. The mean value of this kinetic energy actually represents to the physicist the temperature of the molecules or particles concerned. For a given type of molecule or of particle the velocity increases with rise of temperature, $m$ being constant.

Now consider a suspension of colloidal particles in water at a given temperature. Since the temperature of the colloidal particles is the same as that of the water molecules their average kinetic energy must also be the same. The same is true of any other particles at that temperature provided they are free to move independently of one another. We can write $\frac{1}{2} m_1 v_1^2 = \frac{1}{2} m_2 v_2^2$ where $m_1$ and $v_1$ refer to water molecules, $m_2$ and $v_2$ to colloidal particles. Thus if, as in our case, $m_2$ is much greater than $m_1$, then $v_1^2$ must be greater than $v_2^2$ in the same ratio. Hence the average velocity of large particles is less than that of small ones.

**Diffusion.**—We may now study the manner in which a colloidal particle can get from place to place in a liquid. Suppose that, on the average, it can get from a point A to a point B in $t$ seconds. Its actual path will be a very complicated one, composed of a vast number of short paths in all directions as it is driven hither and thither by collisions with molecules of the liquid. Its true average velocity can therefore not be arrived at by taking the distance AB and dividing by the time $t$. It is obvious, in spite of this, that other things being equal, the time $t$ taken in getting from A to B will decrease as the true velocity increases, so that small particles, which have a higher true velocity, will also be quicker than large ones in getting from place to place. Now this capacity for getting from place to place is simply what the chemist calls *diffusion*. Large particles will therefore have a smaller rate of diffusion than small ones. Comparing, in this way, colloidal particles with, say, molecules of sugar at the same temperature it is found that the former diffuse so much more slowly than the latter that measurement is very difficult. Indeed, for many years it was accepted as a characteristic of colloidal particles that they do not diffuse.

**Dialysis and Ultrafiltration.**—The large size of colloidal particles in comparison with molecules of water and of substances in true solution, is of great practical importance. It enables colloids to be freed from dissolved molecules in two ways. In the first, called *dialysis*, the colloidal system is contained in a membrane which is placed in pure water. The membrane is of some substance, such as parchment or collodion, which allows the passage of dissolved molecules and water molecules but whose pores retain the colloidal particles. The outward diffusion of the dissolved molecules gradually removes them. In the second method the colloidal system is placed on a specially prepared filter with extraordinarily fine pores through which the liquid is forced. The colloidal particles remain behind and can be washed with pure water. This is described as *ultrafiltration*. It is possible to prepare collodion ultrafilters with a graded series of pore sizes.

**Osmotic Pressure.**—Interesting effects arise when molecules or particles are prevented from diffusing by a membrane which will not allow them to pass, but which offers no obstacle to the molecules of the solvent. Such a membrane is described as *semi-permeable*. Let us suppose, to take a concrete example, that on one side of such a membrane we have pure water, on the other side, a dilute sugar solution. The tendency is for the sugar molecules to diffuse from the solution to the pure water. They are prevented from doing this by the membrane, which they cannot pass. However, the same final effect, namely, an increase in the average volume of liquid for each sugar molecule can equally well be attained if pure water passes into the sugar solution. This movement therefore begins and if not opposed, it would eventually lead to an infinite dilution of the sugar solution. The movement can, however, be completely stopped by applying to it a pressure which would cause liquid to move through the membrane from the sugar solution to the water with the same speed as the water which is moving in the opposite direction. When equilibrium has been attained in this way the applied pressure measures the osmotic pressure of the sugar molecules. Now it is found that osmotic pressure and gaseous pressure are governed by the same laws, both qualitatively and quantitatively. Thus a given number of gaseous molecules enclosed in a fixed space at a fixed temperature exerts a definite pressure which is independent of the size of the molecules. This is a direct consequence of the fact that all gaseous molecules at the same temperature have the same kinetic energy. Precisely the same thing is found with molecules in solution, the osmotic pressure being independent of the size of the molecules. Further, considering a given space at a given temperature, the osmotic pressure and the gaseous pressure are exactly equal for the same number of molecules. Thus at 0° C. an osmotic pressure of 1 atmosphere (760 mm. of mercury) is given by 1 gramme molecular weight of sugar or of any other similar substance which is dissolved in 22·4 litres of solution. (It will be remembered that 1 gramme molecular weight of any gas has at 0° and 760 mm. a volume of 22·4 litres.) Now the number of molecules in 1 gramme molecule of any substance is known and is given by the colossal figure of $60{\cdot}6 \times 10^{22}$. This number of molecules, therefore, whatever their size, will always produce an osmotic pressure of 1 atmosphere when dissolved in 22·4 litres of any suitable solvent at 0° C. Since, as we have seen, a colloidal particle has the same kinetic energy as a molecule, it would appear that $60{\cdot}6 \times 10^{22}$ colloidal particles of any kind in 22·4 litres of colloidal solution, that is $2{\cdot}7 \times 10^{19}$ per c.cm., should give an osmotic pressure of 1 atmosphere. If, now, we consider an actual example, we shall see how this works out in practice. Few colloidal systems, even amongst those with high concentrations of small particles contain more than $10^{16}$ particles per c.cm. Even in such favourable cases the osmotic pressure will thus scarcely exceed one three-thousandth of an atmosphere, equivalent to a head of water of only 3 mm. Hence colloidal solutions in general have small, in most cases scarcely measureable, osmotic pressures. The small osmotic pressure unlike the low rate of diffusion, is not a consequence of the large size of colloidal particles in comparison with molecules, but is purely due to their comparative fewness in number. (It is necessary to emphasize this point because the low rate of diffusion and small osmotic pressure of colloids are often mentioned together as though they were both manifestations of the same fundamental property.)

**Coagulation.**—We have seen how the collision with molecules of the liquid produces Brownian movement in the suspended particles. We must now consider the effects which follow when the latter collide with each other. There are three possibilities. Firstly, the collisions may all be of the billiard-ball type in which the particles immediately move away after touching. This type of collision will obviously lead to no permanent changes in the system and the total number of particles present at any time will be constant. The colloidal system is perfectly stable. Secondly, the collisions may all lead to union between the particles, which then adhere firmly together. Under these circumstances there will be a continual decrease in the number of independent particles and a continual increase in their average size. This process is termed *rapid coagulation* (or *flocculation.*) Thirdly, some of the collisions may be effective in causing union between the particles and others not. This coagulation will be a slower process than that considered above, and it is usually referred to as *slow coagulation.* We shall see later how the addition of increasing amounts of salts has the power of bringing a stable colloidal system first into the region of slow coagulation and then into that of rapid coagulation. At the moment we are concerned with the coagulation process itself rather than with the factors which cause it.

Fortunately the process of coagulation has not only attracted the attention of chemists, but also that of mathematicians. Starting with four simple assumptions the latter were able to deduce all the important features of quick coagulation. The assumptions were (1) that the colloidal particles were all small spheres, (2) that they were all of the same size, (3) that their only motion was the random Brownian movement, and (4) that all collisions led to union between the particles. The deductions arrived at, which have since been abundantly verified by experiment, were (1) that the speed of coagulation is independent of particle size, depending only on the properties of the liquid and on the number of particles per unit volume, (2) that particles do not attract one another from a distance and can only exert force on each other at the very instant they touch, (3) that the average volume of liquid available for each particle increases as coagulation proceeds in direct proportion to the time measured from the beginning of the coagulation process.

Now it is unusual for the agriculturist to deal with colloidal systems so perfect that they fulfil all the conditions laid down above. For instance, systems containing particles all of the same size and shape are rare, and we may therefore expect that the equations of the mathematicians will seldom be obeyed. Fortunately, something is known of the coagulation process when the particles are of different sizes. The effect is to make the coagulation more rapid, because the chance of a small particle colliding with a large one is greater than that of two identical particles colliding. The tendency therefore in such a mixed system is for the smallest particles to form a coating around the larger ones. This coating is, as we shall see later, of great importance in soils where practically every size of particle is represented. Again, it often happens that the particles concerned are not spherical in shape. In extreme cases they may be like thin plates or long rods. It has been shown that plate-shaped particles coagulate only a little more quickly than spherical ones, but that long rod-shaped particles may coagulate with enormous speeds. It is for this reason that the clotting of blood occurs so quickly. Blood contains a colloidal protein known as fibrin, whose particles are rod or needle-shaped, and it is the quick coagulation of these particles which causes the sudden change from the fluid blood to the jelly-like clot.

Further, cases also occur in which the particles which are coagulating move together in some definite direction in addition to executing their random Brownian movement. An instance of this is in the rising of cream to the surface of the milk. The fat globules of milk, being lighter than water, all tend to move upwards. Since they move with different speeds according to their sizes (as we shall see later), many further collisions are rendered possible apart from those caused by Brownian movement, and the coagulation proceeds more quickly in consequence. We shall consider this instance in greater detail in discussing the colloidal properties of milk. A similar effect is also found in the flocculation of soil suspensions by calcium salts, but in this case the motion is downwards since the soil particles are heavier than water. Coagulation which is accelerated in this way by motion in one direction is termed "*orthokinetic.*"

**Settling under Gravity.**—Most people are aware that substances denser than water tend to fall through it and those lighter to rise through it under the action of gravity. Common observation teaches that large objects move downwards or upwards in this way more quickly than small ones. Here, again, the mathematicians have added precision to our knowledge and have given equations connecting the speed of fall with the size of the particle concerned, its shape, the difference in density between it and the liquid, and certain properties of the liquid. The simplest case is that of a spherical particle of radius $r$ and density D moving in a liquid of density $d$. Its velocity under gravity is then given by $V = K \, . \, r^2 \, (D - d)$, K being a constant for a given liquid at a given temperature. From the formula we see that the speed is very sensitive to change in radius. It falls rapidly as the radius of the particles decreases. When $D - d$ is positive, the particle falls, being heavier than the liquid, when $D - d$ is negative it rises, being the lighter. In order to make the subject more tangible we shall consider two familiar and important examples, the rise of butter-fat particles in milk and the fall of soil particles in water. In Table I are given the velocities of particles of different sizes and also the times taken to traverse 1 cm. of the liquid under the action of gravity. It will be noted that the value of K is less for milk than for water at the same temperature (20° C.), the reason being that skimmed milk is a more viscous liquid than water. In both cases the particles are supposed to be spheres. The density of butter-fat is taken as 0·930 whilst that of the liquid in which it moves is 1·036. The soil minerals are supposed to have a density of 2·65.

Now it will readily be seen from the table that particles of colloidal size ($<200$ m$\mu$) move so slowly that long periods must elapse before the movement becomes apparent to the eye. Indeed in most cases it is not observed at all because very slight differences in temperature between one portion of the liquid and another are sufficient to cause

### TABLE I

Velocities and Times taken for 1 cm. movement of Spherical Particles

| Diameters. | Butter-Fat in Milk. (K = 11,980 (D − d) = − 0·102) | | Soil Particles in Water. (K = 21,713 (D − d) = 1·65) | |
|---|---|---|---|---|
| | V cm./sec. | T | V cm./sec. | T |
| 0·02 mm. | $1·22 \times 10^{-3}$ | 13 m. 40 s. | $3·58 \times 10^{-2}$ | 27 m. 9 s. |
| 0·01 ,, | $3·05 \times 10^{-4}$ | 54 m. 20 s. | $8·96 \times 10^{-3}$ | 1 m. 52 s. |
| 0·005 ,, | $7·64 \times 10^{-5}$ | 3 h. 37 m. | $2·24 \times 10^{-3}$ | 7 m. 26 s. |
| 2 μ | $1·22 \times 10^{-5}$ | 22 h. 47 m. | $3·58 \times 10^{-4}$ | 46 m. 31 s. |
| 1 μ | $3·05 \times 10^{-6}$ | 91 h. 8 m. | $8·96 \times 10^{-5}$ | 3 h. 6 m. |
| 500 mμ | $7·64 \times 10^{-7}$ | 15 d. 4 h. | $2·24 \times 10^{-5}$ | 12 h. 24 m. |
| 200 mμ | $1·22 \times 10^{-7}$ | 94 d. 22 h. | $3·58 \times 10^{-6}$ | 77 h. 32 m. |
| 100 mμ | $3·05 \times 10^{-8}$ | 379 d. | $8·96 \times 10^{-7}$ | 12 d. 22 h. |

irregular currents which are much more rapid than the actual settling of the particles. This is true also of particles in the border-line region between coarse suspensions and colloidal solutions, and very special precautions must be taken to measure the settling of particles with speeds less than $10^{-4}$ cm. per sec. For this reason, therefore, the usual statement that colloidal solutions do not settle may be accepted, although strictly speaking, it is not true.

Turning our attention now to the various kinds of non-spherical particles we need only consider two main types, those which are flattened or plate-shaped and those which are elongated or rod-shaped. Both types occur in soil suspensions. Particles of mica are always present as thin plates, whilst particles of tourmaline or zircon are usually found as rods. The clay minerals themselves, which we shall consider later, are usually plate-like, though not as markedly as mica. It is found that plates and rods move more slowly than spheres of the same volume, the speed decreasing as the plate- or rod-like character becomes more marked.

**Optical Properties.**—We have mentioned in Chapter I that truly colloidal particles are too small to be observed under the ordinary microscope. What does this imply? Take first of all the case of a particle just sufficiently large to be observed under a high magnification by direct light. Such a particle is seen because it causes an appreciable disturbance to the train of light waves which pass from the source of light through the microscope to the eye. A smaller particle would also cause a disturbance, but one so minute as to be swamped by the undisturbed light waves all around it. Now the disturbance caused by a particle is not only manifest in the direction of the beam of light but is even more pronounced at right angles to the beam. If we can observe the effect at right angles we shall eliminate the swamping action of the undisturbed light waves which pass straight on. That is what happens when we see the motes in a sunbeam. The air contains small floating particles of dust. Looking out towards the sun we miss them because the total light from the sun is too bright in comparison with the feeble light scattered from the particles. Looking sideways, however, against a dark background we see them plainly, because the eye receives only this scattered light and none of the direct rays from the sun. An exactly similar effect is obtained with colloidal particles suspended in a liquid. In fact, the readiest means of distinguishing between colloidal systems and true solutions is to expose each to a concentrated beam of light from an arc lamp and observe at right angles. If the beam can be seen in the liquid, then colloidal particles are present. The effect is usually referred to as the Tyndall cone in honour of the physicist who first investigated the properties of light scattered from small particles. When the light is directed into the liquid by means of a convex lens the shape of the beam is, of course, a double cone, and the scattered light is most intense at the apex where the beam is brought to a focus (Fig. 2).

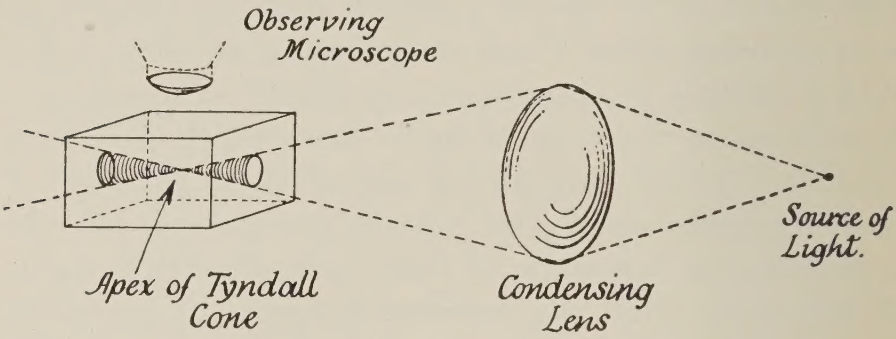


FIG. 2.

It is noteworthy that the Tyndall cone is generally bluish in colour. This is due to the fact that the shorter waves of light in the blue region of the spectrum are much more strongly scattered than the longer red and yellow waves. For this reason also, the solutions giving a bluish Tyndall cone appear orange when held between the white source of light and the observer, as yellow and red rays are able to pass straight through the solution without appreciably weakening in intensity.

Now one of the most momentous discoveries in colloid physics was made in 1903 when Zsigmondy first focussed a microscope on the apex of such a Tyndall cone (Fig. 2). He found that the clear red solution of colloidal gold which he was investigating at the time, showed thousands of brilliant green and yellow particles in vigorous Brownian movement. The ordinary microscope using direct light showed no trace of such particles. A new type of instrument specially suited to this method of observation was quickly developed and was named the *ultramicroscope.* All particles which could be seen as individuals by this means but which were too small to give an image in the ordinary microscope were termed ultramicrons. The size of the smallest particles which can be seen in the ultramicroscope varies enormously with different substances. In the case of colloidal gold, where the conditions are extraordinarily favourable, particles of 5 m$\mu$ diameter have been seen. Yet colloidal clay particles below 50 m$\mu$ in size are very difficult to observe and it is doubtful whether the best apparatus will show clay particles of 20 m$\mu$ diameter.

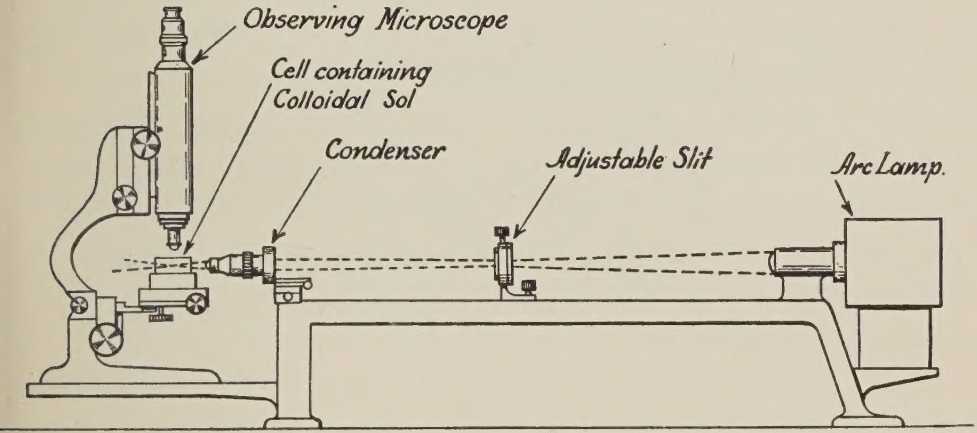


Fig. 3.—The Slit Ultramicroscope.

Two chief types of ultramicroscope are now in use. The first (Fig. 3) is a direct development of Zsigmondy's original type and only differs from it in that the light falls on a rectangular slit and the image of this is focussed in the colloidal solution by a condensing lens, whereas in the original model the light source itself was focussed in the solution. This improvement enables a more sharply defined Tyndall cone to be obtained. The second type of ultramicroscope (Fig. 4) utilizes the principle of ordinary dark-ground illumination which was known to microscopists for decades before Zsigmondy's discovery. Instead of being illuminated by a solid cone of light from a condenser, the object is only permitted to receive rays so obliquely inclined to the microscope axis that they cannot enter the objective, which thus only receives light scattered from the particles. Thus in both types of instrument the particles are seen as bright spots of light against a dark background. For particles less than 200 m$\mu$ in diameter the size of the spot of light obtained is practically independent of the size of the particle, but its brightness is very sensitive to slight changes in size, decreasing rapidly as the volume becomes less.

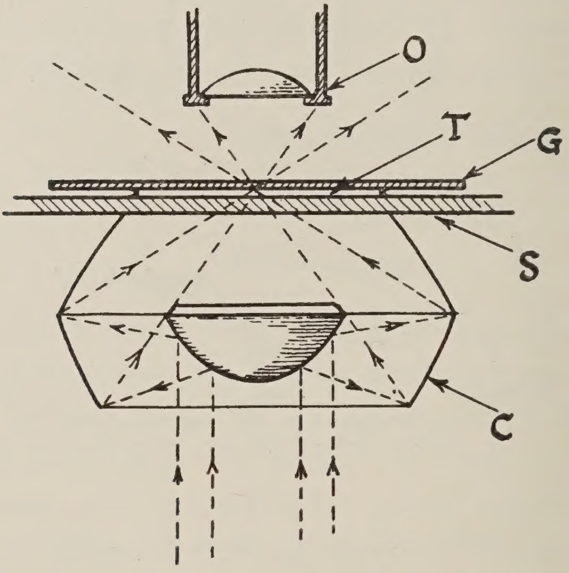


FIG. 4.—The Cardioid Ultramicroscope.

C. Condenser. S. Microscope slide.
T. Thin layer of colloidal sol.
G. Cover-slip. O. Objective.

Both ultramicroscopes can be used to determine the number of particles present in a given volume of colloidal solution. Knowing also the weight concentration of the particles it is easy to calculate their average size, a determination which is naturally of great importance since the diameter cannot be obtained by direct measurement under the microscope.

It will perhaps seem to the reader, at this point, that in learning something of the properties of small particles he has forsaken agriculture and banished all thoughts of the country-side. That need not be so. The farmer who looks out towards the sunset and infers from its appearance the weather of the morrow is gazing at the sun through a disperse system, sometimes a colloidal and sometimes a relatively coarse suspension of particles in the air. Towards evening these particles are chiefly minute drops of water, mixed also with similar particles of dust and soot. As the sun descends to the horizon its rays pass through more and more of this low-lying suspension on their way to the eye. We have seen that colloidal particles scatter blue and green light much more strongly than red. Thus as the sun descends, its light will be deprived more and more of the blue and the green and will become in consequence, a deeper and deeper red. This does not always happen. If the particles encountered by the rays of the sun are microscopic in size instead of being colloidal, the various colours are scattered almost equally. The light appears then white or yellow even at sunset, although its intensity is much less than at midday. The farmer who describes this as a "watery" sunset is expressing in his own way the fact that the air then contains droplets of water which need only grow a little more to descend as rain.

### Supplementary Reading

The topics of this chapter are very fully covered in H. Freundlich's *Capillary and Colloid Chemistry* (London, 1929). Two books are available on mechanical analysis : H. Gessner's *Die Schlämmanalyse* (Leipzig, 1931) and F. V. von Hahn's *Die Dispersoidanalyse* (Leipzig, 1928). The modern work on coagulation has been reviewed by G. Wiegner, *Journ. Soc. Chem. Ind.*, Vol. 50T, page 55 (1931), and by E. W. Russell, *Journ. Agric. Science*, Vol. 22, page 165 (1932).

## CHAPTER IV

## THE PROPERTIES OF MOLECULES AT SURFACES

In discussing the physics of small particles in suspension we have omitted all consideration of the chemistry of surface molecules, the peculiarities of which form the kernal of colloid chemistry. Their importance was emphasized in Chapter I. We must now learn something of their properties. We can best do this by starting from a very simple example, which, incidentally, is of considerable importance to the fruit-grower.

Everyone knows that paraffin and water do not mix, that when they are shaken together a milky liquid results, and that when this is allowed to stand a rapid separation into two layers occurs, the paraffin rising above the water which is the heavier liquid of the two. The condition at the end of such an experiment is the same as it was originally and the shaking has only caused a transient increase in the extent of the paraffin-water interface. Why has the system reverted back to its original condition in spite of the energy expended in mixing the two liquids ? To answer this question we must examine the condition of the molecules on each side of the interface. The water molecules at the interface have a much greater attraction for each other than for the opposing paraffin molecules. Those which are actually in contact with the latter will experience a force exerted by the water molecules behind them which tends to draw them away from the interface. Similarly, there will be a force tending to draw the paraffin molecules away from the interface. Thus there is a very strong tendency on both sides for the interface to become as small as possible under any given circumstances. This effect is usually described as *interfacial tension,* in analogy with the surface tension of a single liquid. The strength of this tendency will naturally vary with different pairs of liquids, being least when the molecules of the two liquids have the greatest attraction for each other.

**The Influence of Dissolved Substances.**—Now the addition of a third substance which dissolves in one of the liquids and not in the other may lead to considerable alteration in the forces acting at the interface. Substances soluble in water, may, for instance, be arranged according to their affinity for the paraffin. Those which have little or no affinity for it will not be attracted to the interface and can thus have little influence on the forces acting there. Salts, acids and bases fall into this category. On the other hand, some molecules soluble in water are strongly attracted to the paraffin. They therefore invade the interface, displacing many of the water molecules and completely altering the balance of forces there. There will now be a much greater attraction between the two liquids and the tendency for the interface to assume its minimum area will be much less than formerly. (Substances which have this effect are described as *capillary-active,* because they reduce the capillarity or inter facial tension.) Many organic compounds are of this type, such as the alcohols, amines, fatty acids, and especially salts of fatty acids, saponins, lipoids, alkaloids and some organic dyestuffs. When an emulsion of an oil in water type is required it is only necessary to add one of these substances to the water before shaking with the oil. The quickest and most economical way to make a paraffin emulsion is to start with a fairly strong solution of soap in water, and to add the paraffin in small quantities at a time with vigorous shaking. A concentrated emulsion is thus formed which can afterwards be diluted with water.

In considering this example we have not, as yet, given any reason why the final result should be droplets of oil suspended in water rather than those of water suspended in oil. It must be confessed that, at present, this aspect of the matter is in a state of some confusion, in spite of many researches on the subject. Certain facts have been established. Sodium, potassium and ammonium soaps always give emulsions of paraffin in water ; these soaps are soluble in water, but not in paraffin. Calcium, magnesium and lead soaps give emulsion of water in paraffin ; these soaps are soluble in paraffin, but not in water. On adding a soluble calcium salt to an emulsion of paraffin in water an interesting series of changes occurs. The first reaction is the formation of the insoluble calcium soap from the soluble sodium soap. This calcium soap now dissolves in the paraffin, the droplets of which, being no longer protected by their coating of sodium soap, begin to coagulate together, forming larger and larger droplets. Eventually the system separates into two layers, a process often described as the "breaking" of the emulsion. On shaking the two layers together, a new emulsion of the water in paraffin type will now be produced, provided there is not present too great a volume of water. This change of type is generally called the *inversion* of an emulsion. Technically it is of some importance, and we shall see later that the making of butter from cream involves such an inversion from the oil in water to the water in oil type.

**The Structure of Capillary-Active Molecules.**—We may now profitably discuss the properties of these capillary-active molecules which have so great an effect on the chemical forces at an interface. From what has gone before it appears that such molecules must contain two contrasted parts, one part being attracted to the molecules on one side of the interface, the other to that on the opposite side. In the soaps, for instance, the metal atom and the —COO— group are attracted to the water molecules whilst the long — $CH_2CH_2$ — — — $CH_2CH_3$ chain is attracted to the paraffin molecules which have a similar chemical structure. The greatest effect is obtained with molecules having a strong lateral attraction for each other. Such an attraction enables them to arrange themselves in a particularly rigid manner at the interface. It is for

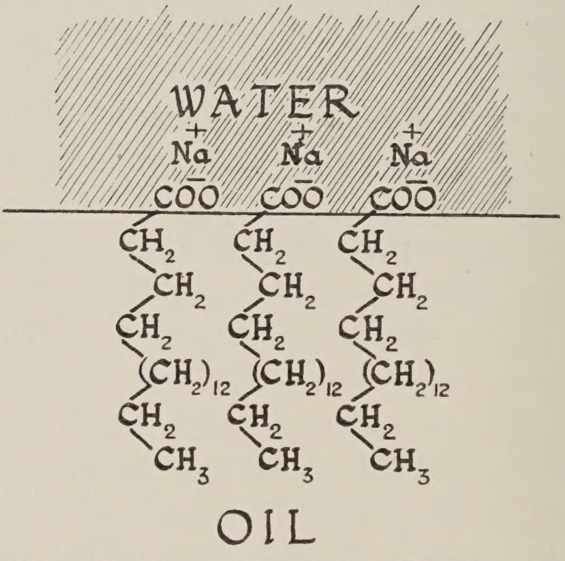


Fig. 5.—Sodium Stearate Molecules at the Oil-water Interface.

this reason that sodium palmitate, with a long hydrocarbon chain of 15 carbon atoms is much more effective than sodium caproate with a similar chain of only 6 carbon atoms. The long hydrocarbon chains have great lateral attraction for each other, so much so that at the water-air interface they are certainly all arranged parallel to one another. The kind of arrangement which probably exists is shown in Fig. 5. It will be noticed that there is only a single layer of soap molecules at the surface. This is described in modern textbooks as a *monomolecular* film, and it is an exceedingly common type, although it is not safe to assume that all dissolved substances form single layers of molecules at an interface.

**Absorption and Adsorption.**—Before proceeding to the discussion of other types of surface effects we must become acquainted with the exact meaning of the different terms used to describe the accumulation of a substance at an interface. When the process is confined to the interface we speak of an *adsorption.* In many cases, however, there is also a penetration of the molecules beyond the interface. This is termed *absorption,* but often this word is used to describe the whole process, that is, the formation of the adsorbed layer as well as the subsequent penetration. It has been suggested that to avoid confusion the word *sorption* should be used for the general process without reference to its mechanism, adsorption for the surface accumulation only and absorption purely for the subsequent penetration into the interior if this should occur.

**Molecules at the Solid-Liquid Interface.**—Having dealt at some length with the properties of the liquid-liquid interface we may dismiss the solid-liquid interface rather more briefly, although the experimental studies of this type have been much more numerous than those of the former type. A solid surface is characterized by the rigidity of its molecules, which may either be arranged in a definite pattern as they are in all crystals or arranged at random as they are in the truly amorphous substances. We are now beginning to realize that the terms "colloidal" and "amorphous" are very far from being synonymous. Many fine precipitates which were formerly described as amorphous have been shown to be essentially crystalline, the crystals being of colloidal dimensions, and possibly less perfectly developed than the larger crystals of the same substances. Now the adsorption of a substance at a crystalline surface must depend both on the molecules present and on their arrangement and spacing. Since these last differ according to the faces shown by different forms of the crystal, it will be expected that adsorption will not be uniform over the whole surface. In dealing with crystals of colloidal size we have no means of estimating the adsorption on the different faces and what we measure is a mean value.

The best-known example of a substance with a high power of adsorption both for molecules in solution and as we shall see later, for gases, is that of charcoal. Animal charcoal has long been used by the organic chemist for removing the dark-coloured and undesirable substances of high molecular weight from his preparations. It finds many technical applications of a similar kind, especially as its powers of adsorption are not confined to the substances of high molecular weight. Purer forms of carbon, such as specially prepared ash-free charcoal, show similar powers of adsorption. Now this high adsorption is due to the enormous internal surface exhibited by these forms of carbon. We may regard a colloidal system of this kind as being sponge-like, a solid foam, as it has sometimes been called. The structural units from which this irregular framework is built up are very small ultramicrons of graphite, and the method of preparation combined with the high melting-point of carbon prevents these units from growing into large crystals. The internal pores represent the space formerly occupied by the hydrogen, oxygen and nitrogen atoms in the organic material from which the carbon has been prepared. The properties of charcoal make it an ideal substance for experiments on adsorption reactions and the laws by which they are governed. These last may briefly be summarized as follows :

(1) True adsorption takes place very quickly and an equilibrium is then immediately established between the adsorbed molecules on the surface and the free molecules in solution. When substances are slow in reaching equilibrium it is a sign that some secondary process, such as an absorption, is following the adsorption.

(2) As the concentration of the molecules in solution increases the amount adsorbed also increases, at first quickly, then more slowly, until finally a saturation value is reached beyond which no further quantity can be adsorbed. Various equations have been put forward to express this relationship.

**Reactions of Adsorbed Molecules.**—The properties of molecules which are held at a surface by adsorption may be markedly different from those of similar molecules in solution. It has been shown, for instance, that hydrochloric acid molecules which are adsorbed on charcoal have lost the power of dissociation into hydrogen and chlorine ions which they possess in solution. In this case the chemical reactivity of the molecules has been decreased by adsorption. In other cases, however, it may be enormously increased; as when alcohol vapour is adsorbed on platinum black and then reacts spontaneously with the oxygen of the air (Döbereiner's Lamp). The increased reactivity of adsorbed molecules affords the reason why finely divided substances act as *catalysts* in many reactions. In such cases the reaction goes wholly at the surface, where the adsorbed molecules are not only more reactive than in solution but are also at a higher concentration. The use of catalysts has revolutionized chemical industry during the present century. The production of sulphate of ammonia by the modern synthetic process depends entirely on the efficiency of a catalyst in promoting the combination of nitrogen and hydrogen. Similarly, the hardening of vegetable oils to make fats suitable for margarine depends on the catalytic power of finely divided nickel, which promotes the combination of the oil with hydrogen. But the most astounding examples of catalytic activity are those which are concerned in biological reactions. These catalysts of nature's laboratory are termed *enzymes* and our knowledge of their properties as colloids is still extremely scanty.

We have here no need to go into details of other types of adsorption, such as that of gases at the surfaces of liquids and of solids. We may, however, conclude this section by considering the thickness of the adsorbed layer. In discussing the liquid-liquid interface we have developed the subject in a way which suggests that the adsorbed molecules form a layer only one molecule in thickness. Strictly speaking, this has only definitely been proved for the adsorption of certain heavy molecules at the liquid-gas interface. There are circumstances, however, in which layers several molecules thick may be produced—as, for instance, in cases where the adsorbed molecules have a strong attraction for one another. Such molecules are generally associated in solution, forming double, or treble molecules, and since they are often strongly adsorbed we may conclude that the adsorption layer formed may be several molecules in thickness.

The fact that molecules may be associated at an interface brings to mind the further possibility that there may be a dissociation, or splitting up into ions, of adsorbed molecules. This latter case is so important that we shall devote the whole of the following chapter to the general topic of dissociation at interfaces.

### Supplementary Reading

On the subject of adsorption, H. Freundlich's *Kapillarchemie* (now translated as *Capillary and Colloid Chemistry*, London, 1929) has been regarded as a classic ever since the first edition in 1909. His *Elements of Colloidal Chemistry* (London, 1925) gives a simple treatment. N. K. Adam's *The Physics and Chemistry of Surfaces* (Cambridge, 1930) gives a very clear account of interfacial tension and of the orientation of molecules at liquid surfaces. E. Rideal's *Surface Chemistry* (London, 1928) should be consulted for an account of catalysis at surfaces and for the mathematical treatment of surface properties generally.

# CHAPTER V

# IONS AT SURFACES

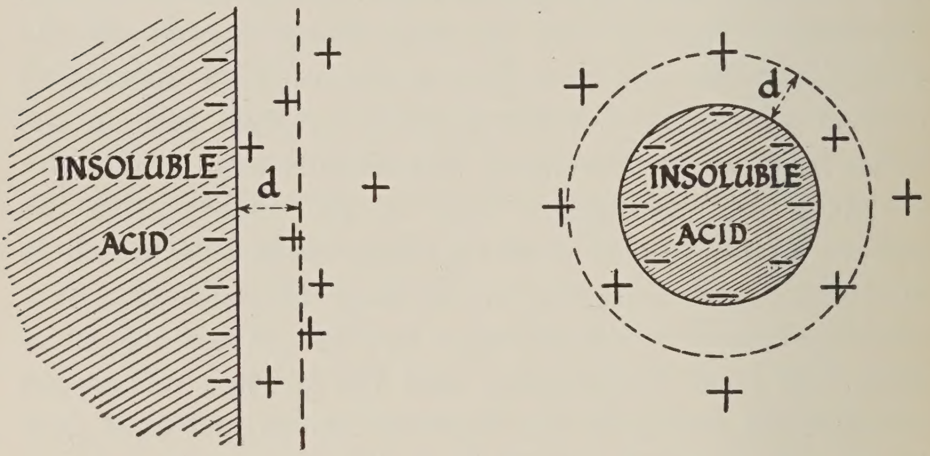
We have touched lightly more than once in these pages on the debt which those who study colloids owe to mathematicians and physicists. Were we to deal historically with the subject of this chapter these lines would resound continually with the names of illustrious physicists; Quincke and Wiedemann, Helmholz, Smoluchowski and Perrin. Indeed, so intensively was the subject studied from the physical side that the chemist had much difficulty in finding some point of contact between the theories advanced and the molecules with which he was chiefly concerned. The reconciliation of view-points has only quite recently been made and we can at last deal with the subject in a simple chemical way. In doing so we shall require to use the modern physicist's conception of the chemical molecule, which will entail a slight digression for the information of those who are unable to keep abreast of the many developments in this field.

**Dissociation.**—What makes the neutral chemical molecule of a salt, acid or base split up into oppositely charged ions? We can best answer this question by taking a simple example. The combination of one atom of sodium with one atom of chlorine to form common salt is really an electrical process. According to our modern views, all atoms consist of two parts—a very small positively charged core or *nucleus* in which most of the weight of the atom is concentrated, and a number of units of negative electricity called *electrons* which rotate about the nucleus and whose total negative charge just balances the positive charge of the nucleus. These electrons are in concentric layers around the nucleus, the number of such layers increasing with the atomic weight. The outermost layer of all contains what are known as valency electrons. These, and these only, can pass from one atom to another during chemical changes. The sodium atom has its electrons in three layers ; two in the innermost, eight in the middle, and a single valency electron in the outermost. The two inner layers of the chlorine are similar to those of the sodium, but the former differs by having seven valency electrons in its outermost layer. Whenever possible it captures a valency electron from another atom in order to form a complete shell of eight electrons. In sodium chloride, therefore, one electron belonging to the sodium atom has passed into the keeping of the chlorine atom so that the sodium has now become a sodium ion with a positive charge and the chlorine atom has acquired a negative charge and become a chlorine ion. A molecule of sodium chloride consists, therefore, of a positively charged sodium ion attracting a negatively charged chlorine ion. But why should such a stable union both from the chemical and electrical point of view become so far loosened that the two ions can move away from one another and behave quite independently, as they do when the molecules are dissolved in water ? Evidently the water itself is seriously affecting the union between the two ions, yet the ordinary conception of water molecules as being made up of two electrically neutral hydrogen atoms and one electrically neutral oxygen atom gives us very little assistance in forming a mental picture of the process. Now the modern view is that each hydrogen atom gives an electron to the oxygen atom so that although the whole molecule of water is an electrically neutral thing, the neighbourhood of the oxygen atom will be under the influence of its acquired negative charges and the neighbourhood of the hydrogen atoms will be under that of their positive charges. It amounts to this, that different parts of the water molecule have different electrical properties which we represent $(H_2)^+ - O^-$. When such molecules come into contact with the somewhat similar ones of sodium chloride $Na^+ - Cl^-$, there is a tendency for the + part of those water molecules near the − chlorine to be attracted thereby and similarly for the − part of those near the + sodium. The sodium and the chlorine are no longer exclusively employed in attracting each other, and their mutual attraction progressively weakens as more water molecules take part, until it becomes slight enough for them to move independently of each other. Such is the process of ionization.

These ideas help us enormously in discussing the dissociation of surface molecules, because here also we can expect water molecules to behave much as they did for sodium chloride. Three distinct possibilities come to mind. We may have dissociation of some of the original surface molecules themselves, dissociation of some of the adsorbed molecules from solution, or the adsorption of ions from solution. Examples are known of each of these methods by which an electrically charged surface can be produced, but before dealing with individual cases we shall consider the general properties of such charged surfaces, independently of the manner in which the charge has arisen.

**Dissociation at an Interface.**—It will be obvious from the very nature of the process of dissociation that the positive and negative charges in the system must exactly balance each other. If certain of the charges are fixed at definite points on the surface, then an equal number of charges of opposite sign must be present in solution. But whereabouts in the solution shall we find these balancing ions? That is the question which tormented the physicists. We can best form a picture of a dissociated surface by considering the simplest possible case in the same way as we discussed the dissociation of sodium chloride. Let us imagine that we are dealing with the surface of an insoluble, weak, monobasic acid which is in contact with pure water. Because the substance is a weak acid, only a small proportion of the surface molecules will tend to dissociate and the process will go on through the action of the water molecules just as it does in the case of sodium chloride. A hydrogen ion will be forced to leave the surface from each molecule of acid having the power of dissociation. We can imagine that for every thousand surface molecules ten split up, liberating ten hydrogen ions. These ten ions are, however, by no means so free in their movement as were the sodium atoms liberated from sodium chloride. For the latter, wherever they moved, were always in the vicinity of some chlorine ions of opposite charge which would attract them hither and thither in the solution. The dissociated hydrogen ions, on the other hand, are only attracted by the oppositely charged ions attached to the surface, so that the probability of their moving far from the surface is very remote. Yet the continual bombardment by the

Brownian movement of the water molecules will prevent them from staying strictly in one place, and in practice there will be a continual interchange between the ions in solution and the surface, some ions returning to the surface while others are being dissociated. At any instant, however, we may picture the state of affairs as being on the lines of Fig. 6 (*a*). Here the + signs indicate hydrogen ions and the — signs the surface anions of the acid. One hydrogen atom is shown as being on the point of recombining with the surface anion, the others are at varying distances from the surface. As we proceed outwards from the surface we shall encounter at first more and more ions until a maximum is reached and then the number will fall off gradually to zero.



(*a*) (*b*)

FIG. 6.—The Electrical Double Layer at the surface of an Insoluble Acid.

*d* represents the mean thickness.

We have now to consider the ways in which the possession of such a surrounding swarm of ions affects the surface. By dissociation the surface has now acquired a new property—that of carrying an electric current, just as does a solution of sodium chloride. Indeed, if in the example just considered, we imagine the surface to be curved instead of plane (Fig. 6 (*b*)), we obtain a picture of a small colloidal particle whose behaviour towards an electric current will be similar to that of any negatively charged ion. When an electric current is passed through the suspension it will move to the positive pole like the chlorine ion, and the swarm of cations around it will move to the negative pole like the sodium ion of sodium chloride. We have thus built up a simple picture of a negatively charged particle or colloidal anion, which by interchanging the positive and negative charges, would become a picture of a positively charged particle or colloidal cation. Such colloidal ions are called *micelles.*

**The Influence of Ions in Solution.**—We must take care, however, in comparing a colloidal micelle with a dissociated molecule that we do not push the analogy too far. There is a big difference, for instance, between the acetate ion with its one charge and the colloidal particle pictured above, although both arise from the dissociation of weak acids. This difference is well brought out if we consider how the addition of a small quantity of a strong acid like hydrochloric acid can affect the electrical properties of acetic acid on the one hand and a colloidal acid on the other. Acetic acid is so weak that only a small proportion of the total molecules present split up into ions according to the equation $CH_3COOH \rightleftharpoons (CH_3COO)^- + H^+$. A strong acid such as hydrochloric acid is completely ionized in dilute solution and the effect of adding it to the acetic acid is to increase enormously the number of hydrogen ions. Thus the chances of the acetate anion recombining with a hydrogen cation are vastly increased and the number of free acetate ions in solution decreases. But although there is a reduction in the total number of acetate ions, those which still remain have exactly the same electrical properties as they had originally and will move to the positive pole when an electric current is passed at the same speed as they did when no hydrochloric acid had been added. The addition of hydrochloric acid to the suspension of our colloidal acid will reduce the tendency to ionization in the same kind of way, but here the reduction can proceed by steps at the surface of every particle. On the average, therefore, the particles will each experience the same amount of recombination of surface anion with hydrogen cation, leading to a reduction in the negative charge carried by each particle. Now the speed at which a negatively charged particle moves towards the anode depends on the number of charges it carries, so that in the case we have considered, the addition of hydrochloric acid will cause a decrease in the speed of movement of the colloidal particle in an electric field. This, however, is not all. Suppose that our particle having originally ten negative charges and ten dissociated hydrogen ions now has five. Are these five in the same condition as the original ten ? Obviously they are subject to a force which the original ten ions did not experience, namely, the osmotic pressure of the hydrogen ions from the hydrochloric acid which will tend to drive them closer to the surface. The average distance of the remaining five ions from the surface will be less than that of the original ten. It is found that this change also causes a reduction in the speed with which the particle moves in an electric field. Thus the speed of movement of a colloidal particle under a given electric field or the *cataphoretic* velocity, as it is termed, depends upon two factors : (*a*) the charge on the particle and (*b*) the average distance between the surface of the particle and the swarm of ions which balance its charge. Either of these factors will be affected whenever a solution of a salt, acid or base is added to a colloidal system. The measurement of the speed of movement of colloidal particles under an electric field (i.e. of their cataphoresis) is therefore important since it gives a measure of the ionic changes at the surface. It does not, however, enable us to distinguish between the two factors (*a*) and (*b*) mentioned above.

When the amount of electrolyte added to the colloidal system is large then practically all surface ionization is inhibited and the surface becomes uncharged. Particles having an uncharged surface will remain stationary when an electric current is passed through the system. Provided, therefore, that a sufficiently high concentration can be reached, any electrolyte will completely suppress the cataphoretic movement of any colloidal particle. The concentration which is just sufficient to reduce the surface charge to zero varies enormously with different electrolytes and different colloids and we shall consider the reasons for this variation in detail later. At present we must focus our attention on the effects arising when the surface charge has been reduced to zero.

**Electrical Properties and Coagulation.**—It will be obvious that at the instant the charge disappears the colloidal properties which we discussed in Chapter III will not have been altered. The particles will still have the same Brownian movement as before and will still collide with the same frequency. But the mechanism of a collision between two particles in the absence of electric charges will naturally be entirely different from that in the presence of such charges. Fig. 7 will help to make this clear. Two negatively charged particles with their swarm of balancing cations are shown approaching one another. As soon as they are near enough the cations belonging to the two particles exert a mutual repulsive force, thus preventing a true collision and causing the particles to move away from each other. Under these circumstances the colloidal system is perfectly stable. When the electric charge and the balancing ions are absent, there can be no such cushioning effect and the particles will be able to approach much more closely.

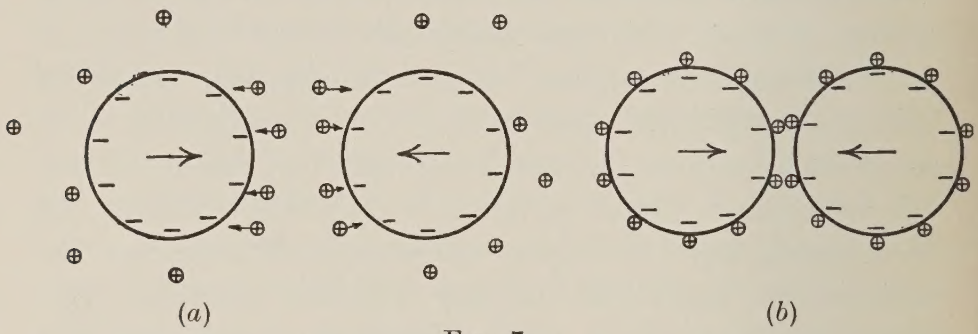


Fig. 7.

(*a*) Charged particles repelling each other as they approach.
(*b*) Uncharged particles coagulating together.

On touching, the surface molecules will mutually attract each other, thus binding them together. In the absence of electric charge all collisions lead to union. We are therefore in the region of quick coagulation. When particles have still some charge remaining it may be sufficient to render a fraction of the collisions ineffective. Here, therefore, a slow coagulation will occur. The relationship between the speed of coagulation and the electrical properties of a colloidal particle is shown in Fig. 8.

Here one curve shows the decrease in the speed of a particle under a field of 1 volt per cm. as the concentration of added acid increases, whilst the other curve gives the number of particles present in the system one minute after the addition of the acid. It will be noted that for small additions of acid there is no decrease in the number of particles, although the velocity has diminished considerably. In this region, therefore, there is no coagulation. Then, at a certain value of the cataphoretic velocity, slow coagulation begins, and its speed increases as the former decreases so that the curve, connecting the number of particles present after a given time with the concentration of acid, shows a rapid fall. This fall continues until the region of quick coagulation is reached, in which the number of particles present after a given time is constant, and here the curve bends round and becomes horizontal. The cataphoretic velocity, mean-

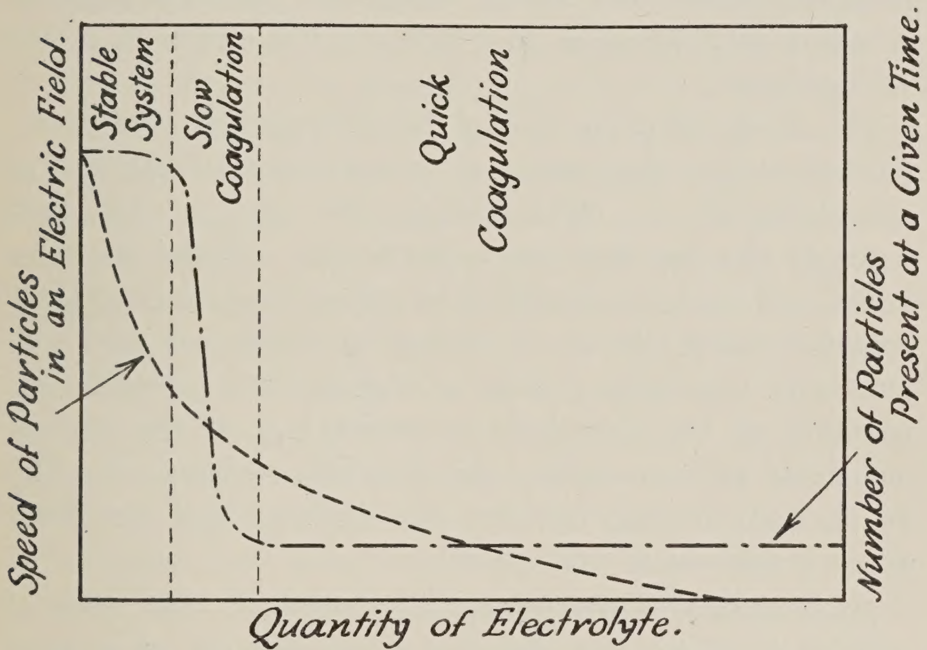


FIG. 8.—Coagulation and Cataphoresis.

while, shows a continuous fall towards zero. There are two concentrations of acid which may therefore be described as "critical." The first is the value for which slow coagulation just begins, the second is that for which rapid coagulation begins. It is found that rapid coagulation may set in while the particle still carries an appreciable fraction of its original charge. In these cases the Brownian movement which brings the particles together is sufficiently vigorous to overcome the electrical forces of repulsion.

The electrical properties of colloidal particles are therefore of major importance in governing the stability of colloidal systems. Other factors also play a part, particularly the chemical properties of the colloidal particles as evinced towards the water or solvent molecules in their neighbourhood. It is convenient to divide colloidal systems into two large groups according to the relative importance of the electrical properties and of the solvent molecules in determining the stability, although it must be understood that between one extreme and the other every gradation is exemplified.

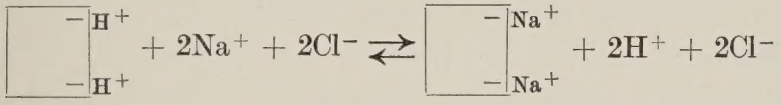
**Hydrophobe and Hydrophile Colloids.**—The class of colloids in which the electrical properties are of preponderant importance, is termed *hydrophobe.* As we should expect, systems of this type are readily coagulated by solution of salts, acids and bases, even at low concentrations. The effectiveness of different compounds in causing coagulation increases with the charge on the ion having the opposite sign from the colloidal particle. Thus in coagulating colloidal gold which is negatively charged, calcium salts act at a much lower concentration than sodium salts; the positive calcium ion having double the charge of the positive sodium ion. Similarly, in coagulating colloidal copper oxide, which is positively charged, sulphates act at a lower concentration than chlorides. Comparing different ions of the same valency such as sodium and potassium, or magnesium, calcium and barium, one finds a slight increase in coagulating power with the weight of the cation. This effect becomes much more marked in colloids tending in properties towards those of the next class, where, as we shall see, it finally overshadows the valency. Within this hydrophobe class a further subdivision is possible, according to the behaviour of the colloid when once it has coagulated. If the solution which caused coagulation is completely removed by washing, then the adhering particles may either remain attached or they may become loosened so that vigorous shaking will redisperse them. Colloids, whose particles when once coagulated remain so, are described as *irreversible*; those which can be redispersed either by simple washing and shaking or by washing followed by addition of some solution which aids dispersion, are called *reversible.* The irreversible colloids are the typical members of the hydrophobe class, showing the greatest sensitivity towards coagulation. The most important of them are the colloidal metals, gold, silver and platinum. The reversible hydrophobe colloids are less typical; they show to some extent properties associated with the next class. Thus they tend to retain water, both at the surface and to some extent in the interior of the particles, and in the coagulated state already show some of the properties of jellies. They are of some importance in biological processes. The colloidal hydroxides of iron and aluminium, many colloidal salts such as the insoluble sulphides and phosphates, all the colloidal minerals which we describe as clays and many organic dyestuffs belong to this intermediate type.

They are sensitive towards coagulating agents, but they can be redispersed by simple means.

The second class is called *hydrophile.* Colloids of this type are of great stability and modification of the electrical double layer has little influence on the degree of dispersion. They are only coagulated by high concentrations of salts, acids and bases and in causing coagulation, the valency of the ion of opposite charge is of less importance than its degree of hydration. The degree of hydration is the average number of water molecules which the ion can hold in virtue of its electric charge. It is found that light ions such as lithium and sodium attract and hold more water molecules than heavier ions such as potassium and barium. In the coagulation of hydrophile colloids the heavily hydrated ions are much less effective than those carrying few water molecules ; hence potassium salts coagulate much better than sodium salts, barium salts than calcium salts, and so on. The reasons for the peculiarities of this class of colloid involve chiefly the chemical properties of all the molecules present, not merely those at the surface of the particles. The molecules which form such colloids have considerable affinity for water as well as affinity for one another. Hence the suspended particles actually contain water, the quantity of which varies according to circumstances. We shall consider the properties of this class in greater detail in the following chapter. It is sufficient to note here that most biological processes are controlled by such colloids.

**Reactions of Surface Ions.**—At an interface, as we have seen, there are two classes of ions. One group forms part of the surface, the other forms part of the surrounding liquid. We may expect, therefore, two kinds of chemical reactions at surfaces ; those which involve the surface ions and those which involve the outer and more mobile ions. It will be obvious that changes of the former type will lead to more drastic alteration in the properties of a colloid than those of the latter type. On the other hand, the outer mobile ions will be the more sensitive to slight changes in the solution, of which they really form a part. We shall therefore deal with them first.

The reactions of the outer, mobile ions are very simple and can readily be appreciated by the use of equations. In these, one colloidal particle is represented by a square or a circle, the fixed surface ions being indicated by their charges and the outer mobile ions by their chemical symbols. The actual number of the latter is seldom known, so that no attempt is made to represent it, and the picture of the colloidal particle and its ions must be taken as purely diagrammatic. For instance, the reaction between a particle of a colloidal acid and sodium chloride would be represented :

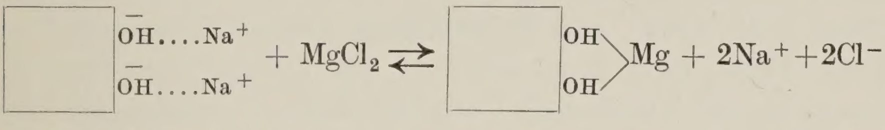


The arrows are used instead of the customary = sign to show that the action is reversible ; that is, the particle having sodium ions in place of hydrogen ions would react with hydrochloric acid just as the original particle reacts with sodium chloride. This means that for fixed amounts of colloid and salt the reaction is never complete, and it can only be made so by removing the liquid in equilibrium with the particles and treating the latter with fresh salt solution. Such successive treatment eventually leads to a complete replacement of hydrogen by sodium. Reactions of this kind are appropriately termed *ionic exchange* reactions ; we can have *cation* or *base* *exchange* with negative colloids as in the above examples, or *anion exchange* where positively charged colloidal particles are concerned. These reactions, at first sight academic, prove to be of major importance to agriculture. They are responsible for the course of soil formation processes, they have considerable influence on the texture of soils and they play a predominant part in the retention and liberation of plant nutrients by soils. We shall therefore return to the subject in Part II.

The replacement of one of the outer ions by another involves two important changes in the general properties of the colloid. We have noted that different ions attract different numbers of water molecules. Those which attract many will obviously be at a greater average distance from the surface than those which attract few. Hence the colloid which possesses heavily hydrated ions will move more quickly under the influence of an electric field than a similar colloid having less hydrated ions. Further, since the outer ions must always accompany the colloidal particles, it follows that when the former are heavily hydrated the latter must appear so. The hydration of colloid particles is therefore affected by the ions in the outer layer.

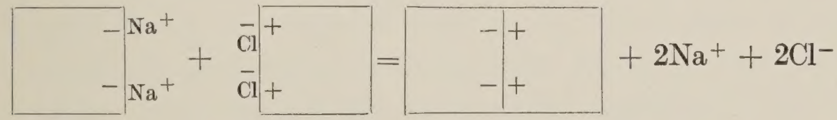
Reactions involving the fixed ions of the surface may be of many kinds. We can only indicate here one important example. It has already been made clear that a surface can acquire an electric charge by the adsorption of ions from solution. One of the most readily adsorbed ions is hydroxyl, $OH^-$. In alkaline solutions many colloids show an increased cataphoresis due to increase of charge by adsorption of hydroxyl. When ions are added which readily combine with hydroxyl ions to form insoluble hydroxides then coagulation very readily occurs;

for the surface then loses its high charge by formation of the insoluble hydroxide. It is for this reason that in alkaline solution, salts of certain metals coagulate at lower concentrations than in acid or neutral solution. We may represent such a reaction thus :



Modification of the fixed ions of the surface is therefore a drastic change which generally involves also the outer ions.

**Mutual Coagulation of Colloids.**—The last topic in this chapter concerns the changes which occur when colloids having oppositely charged particles are mixed. It is not difficult to predict these changes. We have seen that the coagulating power of an ion increases very rapidly with its valency. Now a colloidal particle can be regarded as an ion with a very high charge or valency. Such particles will therefore be highly efficient in coagulating other particles of opposite sign of charge. Since, also, coagulation can occur while the charge on a particle is still appreciable, there will obviously be a considerable range of mixtures of any two oppositely charged colloids for which coagulation will occur. Diagrammatically such a reaction could be represented :



It follows that colloids of opposite sign cannot exist together in suspension as independent particles. We shall see later that many of the theories of soil-forming processes are based on this conclusion.

## SUPPLEMENTARY READING

Here H. Freundlich's *Elements of Colloidal Chemistry* (London, 1925) is more suitable for general reading than *Capillary and Colloid Chemistry* which gives a specialist's account of the subjects of this chapter. Both H. Kruyt, *Colloids* (New York, 1927), and R. Svedberg, *Colloid Chemistry* (New York, 1924), have good accounts, the former more from the chemical, the latter more from the physical standpoint. For the biologist the relevant chapter in R. A. Gortner's *Outlines of Biochemistry* (New York, 1929) is especially important. The most complete account from the chemical aspect is W. Pauli and R. Valko's *Die Elektrochemie der Kolloide* (Wien, 1929).

# CHAPTER VI

## SOLS AND GELS

The colloidal systems which we have so far discussed, display, irrespective of their chemical nature, many properties in common. This is due largely to the purely surface ions and molecules, and in particular to the overriding control exerted by the electrical double layer of ions. But the term colloid was first applied by Graham to quite different systems which we have already described as hydrophile. In these the individual particles contain water, being either granular, sponge-like or felt-like according to their architecture, but in any case being permeable to water molecules and ions from the surrounding solution. Hence the colloidal properties are more largely controlled by the ordinary chemical reactions of their molecules. We find, therefore, in this group the following characters: (1) closely similar colloidal properties in substances of similar chemical nature; (2) diversity of behaviour amongst dissimilar chemical substances; (3) the prevalence of colloidal structures, which may perhaps be regarded as intermediate in type between completely dispersed and completely coagulated systems; (4) the importance of the total amount of water present. We shall appreciate the first two characters later in dealing with particular examples; the third and fourth will serve here as a fitting introduction to the hydrophile colloids.

The change from a fluid to a jelly is familiar to all. Numerous examples are to be found in every cookery-book, illustrating in a picturesque way the habitual deceit which we practise on our appetites. Again, all living things have the power of making jellies to build up and regenerate their bodily tissue. The jellies, or gels as they are scientifically termed, thus transcend all other types of colloids in their biological importance.

Two main types of gels are known. The first class includes all those resembling gelatin; they have the property of swelling in pure water and of producing sols in this way or else by warming without addition of any other substance. Such gels have marked elastic properties and when deprived of a large proportion of their water are tough, elastic solids. In consequence, they are generally referred to as elastic gels. The second class is typified by silicic acid gel. Superficially this has some resemblance to gelatin, but mechanically it is much weaker and on losing water it becomes a brittle solid. It does not take up water readily to form the original gel, nor does the gel itself pass back into the sol unless some dispersing (or *peptizing*) agent is added. Such gels are described as non-elastic.

**The Sol-gel Transformation.**—The substances forming elastic gels pass from the sol to the gel state and vice versa with the greatest facility. Cooling and concentration tend to give gels, warming and dilution to reverse the process, producing sols. The passage of a sol into a gel on cooling is, however, a distinctly different process from the solidification of a pure liquid. The latter will melt again at the same temperature when heat is applied. An elastic gel, however, requires heating to some temperature considerably above that of its formation before it passes back into the sol. This type of lag, or hysteresis as it is called, shows itself in many properties of gels, both elastic and non-elastic, and to some extent also in hydrophile sols.

The non-elastic gels are produced from the corresponding sols in a variety of ways. Coagulation by salts, acids or bases transforms hydrophile sols into gels. In some cases the removal of substances which act as peptizing agents causes the formation of a gel. Ferric hydroxide sols which are rendered stable by a little hydrochloric acid can be coagulated to form a gel when the acid is removed by dialysis. Concentration of a sol eventually leads to a gel. Quite recently sols have been prepared which pass into gels spontaneously when allowed to stand in quietude. As soon as the resulting gel is shaken it passes again into the liquid sol. The process can be repeated indefinitely, and although the phenomenon is at present somewhat of a scientific curiosity it may prove to be of considerable biological importance. (This property has been given the name *thixotropy.*)

**The Properties of Hydrophile Sols.**—Before discussing the special properties of the gels it is important that the differences between the hydrophobe and the hydrophile sols should be understood. The peculiarity of the hydrophile sols lies in the marked effect which the presence of the colloidal particles has on the fluid properties of the water in which they are dispersed. The *viscosity* (which is a measure of the friction between two layers of liquid moving at different speeds) of hydrophobe sols is only slightly different from that of water, and changes such as coagulation have little influence on it. That of hydrophile sols may be many times greater than the value for pure water. It increases rapidly both with the concentration of the hydrophile particles and also whenever coagulation is caused. The increase in viscosity caused by coagulation is measurable even at very low concentration of the sol, and it has been used by many workers to indicate when coagulation has occurred.

The hydrophile sols, particularly those of high viscosity, show also elastic properties akin to those of the gels, which are entirely absent from the hydrophobe sols. A pure liquid which has been set in rotation in a cylindrical vessel gradually comes to rest and then remains stationary. Many hydrophile sols show a small movement after they have come to rest, in a direction opposite to that of the original rotation. To this extent, therefore, the liquid is behaving as an elastic solid, forecasting as it were, the gel state from which it is not far removed.

**Protective Action.**—The special properties of hydrophile sols are strikingly displayed when they are mixed with hydrophobe sols. Two cases arise. If the sign of the electric charge is the same for both types of particle, then the hydrophile sol is strongly adsorbed by the hydrophobe particles. This adsorption may be regarded as analogous to that of any substance of high molecular weight at a surface, the hydrophile particles, which are generally much smaller than the hydrophobe ones, being treated as large molecules. In this way a coated particle is formed which will show the colloidal properties of the outer, hydrophile layer. It will be coagulated only under circumstances in which the pure hydrophile sol would coagulate. In general, as we have already noted, the hydrophile sols are much less sensitive to coagulating agents than the hydrophobe, so that the effect of the coating is to protect the hydrophobe particle from coagulation. The most effective protective colloids are those which form elastic gels, such as gelatin and starch.

Where the hydrophobe and hydrophile sols are oppositely charged, the first tendency, as we would expect, is for a mutual precipitation to occur. This has actually been observed for very small concentrations of the hydrophile particles, but normally they are so far in excess that the unstable complex particles first formed are able to adsorb more of the hydrophile sol and so acquire a complete coating. In this way the hydrophobe particles become fully protected, with the surface properties of the hydrophile sols only.

**Water in Gels.**—The exact function of water molecules in gels is at the same time one of the most interesting problems of colloidal chemistry and one of the most important in plant and animal physiology. In the gels we have the impression that not all the water molecules are in the same state, but unfortunately we have no experimental means of segregating them into classes, and our conclusions are entirely based on experiments involving all the water molecules present. Further, no direct methods are available for measuring the attractive forces between the water molecules and those of the gel substance. These attractive forces, however, govern the tendency for water molecules to escape from the surface, which is readily measured by determining the pressure of water vapour in equilibrium with the gel. By carrying out such measurements when different amounts of water are present we arrive at the vapour pressure curves. These are of different shapes according to the manner in which the water molecules are held. Consider first of all two very simple cases.

(1) All the water molecules are chemically combined with the solid, forming a definite hydrate such as $CuSO_4.5H_2O$. In this case the vapour pressure curve is

that of 1, Fig. 9. The anhydrous solid has no vapour pressure, but as soon as a trace of water is added the hydrate is formed and the vapour pressure remains constant until all the solid has been transformed into hydrate. A little excess water then produces the saturated solution which has a higher vapour pressure than the hydrate, causing a sudden jump in the graph. Further quantities of water go to form saturated solution until all the solid is dissolved, the vapour pressure again being constant. Lastly, still further additions of water dilute the saturated solution and the vapour pressure rises steadily and gradually approaches the value for pure water.

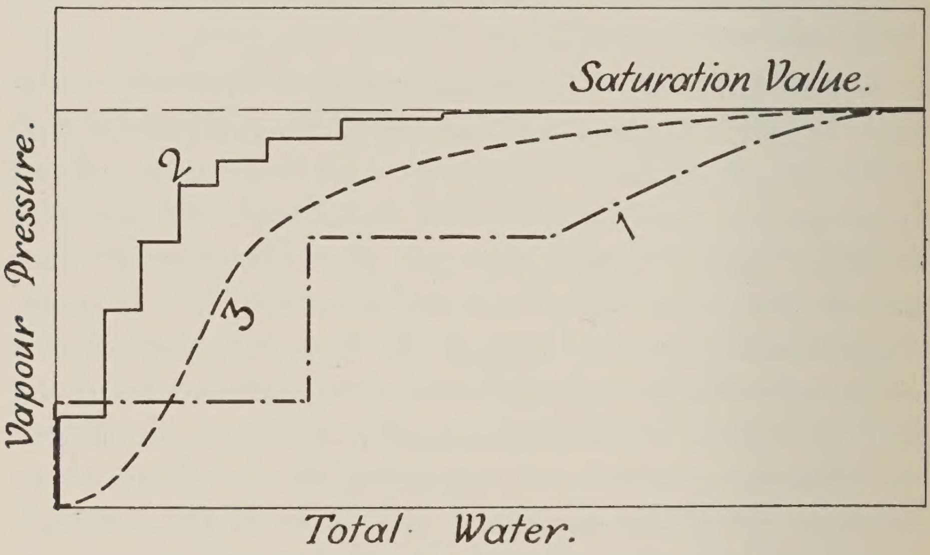


FIG. 9.—Vapour Pressure Curves.
1. A hydrated Salt.
2. Adsorption in steps at a Plane Surface.
3. A typical Curve for a Gel.

(2) The water molecules are adsorbed at the plane surface of the solid. In this case the theoretical curve is of the form shown in 2, Fig. 9. The first additions of water to the dry surface should build up a single layer of molecules

and the vapour pressure will remain practically constant until this is completed. The second layer, being held only by water molecules of the first layer, will have a considerably higher vapour pressure. As succeeding layers are added, the increment of vapour pressure will become less and less until the outermost layer has a value indistinguishable from that of water. The vapour pressure curve will thus consist ideally of a series of decreasing steps, which under the crude conditions of experiment always appears as a moderately smooth curve.

The conditions in an actual gel must be very complex. Excluding the formation of definite hydrates, the whole group of structural details which make up the colloidal architecture of the gel have some influence on the mobility of the water molecules and hence on the vapour pressure. For instance, the internal surfaces will certainly not be plane, they may be both convex and concave. Water molecules may not be able to reach the internal surfaces freely and may set up internal pressure in taking up their positions, thus initiating an expansion of the gel as a whole.

The simplest type of vapour pressure curve is given by the elastic gels such as gelatin, in which the uptake of water molecules causes a continuous increase in the volume. Many other naturally occurring colloids give similar curves. The general shape is that of a sloping letter S (3, Fig. 9).

Much more complex curves are given by certain of the non-elastic gels, notably by silicic acid. Here the peculiarities arise from the fact that after a certain stage of dryness is reached, the gel is no longer able to take up water reversibly and to pass back to its original moist condition. In other words, the partially dried gel has attained a structure which is too stable for the added water molecules to disrupt. Thus the vapour pressure curve for increasing water content is different from that for decreasing water content.

As an illustration of the importance of the water relationships of gels in biology (and no less in agriculture) we shall consider the question of the resistance of plants to drought and to frost. Most of the work on these topics has been carried out in America where the climate compels the farmer to select both his crops and his varieties of a single crop with close regard to these factors.

**The Winter Hardiness of Plants**—It has long been known that the seeds of many plants as well as the spores of some bacteria can survive the experience of very low temperatures. Formerly, it was thought that this hardiness was due to the small water content and that the water present was chemically combined with the material of the seed or spore. The interesting experiments of R. Newton from 1922 onwards have thrown a fresh light on these facts and on the general capacity of plants to resist frost. A number of varieties of autumn-sown wheat were under observation. Samples of the leaves were taken on various dates from October onwards. In order to obtain the sap, the leaves were frozen in ice and salt and then thawed, the sap being extracted by pressure. During October and November no difficulty was experienced in getting quantities of sap from all the varieties, but in December the hardiest gave little sap whereas the non-hardy varieties gave only a little less than formerly. Now the total water content of all the samples was much the same in December as in October. From this experiment two conclusions were drawn; firstly, that in winter the sap water of the hardy varieties did not freeze, and secondly, that wheat plants adapted themselves to winter conditions by transforming water into some form which did not produce ice at low temparatures.

Now it is already known that the production of ice crystals in gels often begins several degrees below the freezing-point of pure water, and that with increasing concentration of the gel the freezing-point drops still further. Finally, a concentration may be reached beyond which no separation of ice crystals can be observed even with very low temperature. These observations are very closely linked with the vapour pressure curves of gels which we have already discussed. It can be proved that a simple proportionality exists between the lowering of the vapour pressure of a liquid and the depression of its freezing-point. Thus if a gel freezes at −3° C. we can calculate immediately its vapour pressure. The same underlying cause governs the departures from normality both of the vapour pressure and the freezing-point. This cause we have already discussed. Water molecules at surfaces may, as we have seen, be expected to show abnormal properties, one of which is a diminished vapour pressure. Now the gels behave as solids with enormous internal surfaces. It would appear possible, therefore, to separate the water occurring in gels into two categories ; interfacial water or *bound water*, and free water. Unfortunately, such a division is entirely arbitrary, since the vapour pressure curve shows no sudden breaks ; but in spite of this the term " bound water " is frequently employed because it conveys a useful impression to the mind.

We may sum up Newton's experiments by saying that the winter hardy plants have a great capacity for transforming the free water of their sap into bound water as soon as colder conditions arise. The exact mechanism of this change is not yet understood.

**Drought Resistance.**—In many ways resistance to drought is similar to winter hardiness. A plant which thrives in a hot, dry climate must fulfil two conditions. Firstly, the rate at which it loses water by evaporation from the leaves must be very small ; secondly, it should be able to take up water vapour from the air when the latter attains a greater humidity than usual. In other words, the cell sap must have a low vapour pressure ; or a high percentage of its water must be in the " bound " state.

Newton has confirmed these deductions. He finds, for instance, that Timothy, having only about 1 per cent. of " bound water " is unable to stand the hot summers of Western Alberta, whereas the Western Rye Grass with 6–10 per cent. of " bound water " is much better suited to the conditions. The figures for " bound water " are minimum values.

The subject of water relationships in plants promises, therefore, to be of first-class importance in agriculture. Its further development will depend largely on the progress made by the colloid chemist in the elucidation of the complex water-gel equilibrium, which has been presented above in its simplest outline.

## SUPPLEMENTARY READING

H. Freundlich's *Capillary and Colloid Chemistry* (London, 1929) gives a full account of the gels, and H. Kruyt's *Colloids* (New York, 1924) may also be recommended. Newton's experiments on winter hardiness have been published in the *Journal of Agricultural Science* from 1922 onwards and they are ably summarized by R. A. Gortner in his *Outlines of Biochemistry* (New York, 1929), where the water relationships of gels are very fully discussed.

# PART II

# *COLLOIDS IN THE SOIL*

## CHAPTER VII

## THE MINERAL COLLOIDS OF SOIL

With the exception of the very purest sea-shore or wind-borne sands, all soils contain particles of colloidal size. These are conveniently divided into two large groups, the inorganic or mineral colloids and the organic or humus colloids. In amount every possible variation is found, and we shall have occasion to discuss these variations later in Chapters IX and X. Besides these two groups of colloids and omitting all living matter from consideration, three other categories of substances are usually present in soils. They are: (1) mineral grains, and fragments of rocks which may be of any size from 1 $\mu$ upwards; (2) water containing various salts in solution; (3) air which owing to the activity of micro-organisms is often abnormally rich in carbon dioxide. But as most people know, plants can grow quite healthily in water culture from which the mineral grains, the inorganic colloids and the organic colloids of soils are all absent. These must therefore play an indirect rôle in plant life by acting both as a mechanical support and as a reserve from which the essential plant nutrients can be drawn. This last aspect has been most intensively studied and it was soon realized that the retention and liberation of plant nutrients were mainly due to the two classes of colloids present. The insistence of the agriculturist on the importance of these properties has led to a seriously lop-sided development in the scientific study of soil colloids; because the question posed has always tended to be "How do they behave?" rather than "What are they?" It is only within the last ten years that a real start has been made with the second question which from a purely logical standpoint should have been attempted first.

The agriculturist, however, has not been the only interested party, and to some extent the blame for the scanty progress made in elucidating the character of the mineral colloids of soils must be shared by the geologist. On all sides the fact that the smallest mineral particles of soils were described as clay colloids hindered their identification because for many years colloids were wrongly regarded as necessarily indefinite in composition and non-crystalline. We now know that practically all the colloidal mineral particles of soils are crystalline, however small they may be. The results of chemical analyses of clays, which can rarely be interpreted by any simple formula, do not really prove that the soil colloids are indefinite in composition. Most soil colloids, like most rocks, are mixtures of different minerals, and it is a great pity that the use of the word colloidal should have obscured this simple fact.

**Mechanical Composition.**—In 1927 the International Society of Soil Science laid down a detailed procedure for the grading of soil mineral matter into fractions according to particle size. The agreed diameters were: 2 mm.–0·2 mm., coarse sand; 0·2 mm.–0·02 mm., fine sand; 0·02 mm.–0·002 mm., silt; less than 0·002 mm., clay. Since soil particles are of irregular shapes these diameters refer to imaginary spherical particles having the same rate of fall in water as the soil particles considered. The dimensions so defined are therefore usually described as *equivalent diameters.* It will be noticed that the upper limit of the clay fraction is 2 $\mu$, whereas that of truly colloidal region may be taken as 1 $\mu$ or even lower. The clay fraction is therefore not wholly colloidal, although it is often referred to as though it were.

The grading of the soil into fractions, or mechanical analyses as we now call it, had been carried out by a variety of methods and with many different limits for the fractions during the past fifty years. The object was twofold. The splitting up of a soil into such fractions facilitated the study of its minerals and therefore helped in elucidating its origin and history. But to the agriculturist the actual quantities of the different fractions present were even more important, because they could be used to express in figures soil properties which had from time immemorial been described by such words as light, loamy and heavy. These refer to the texture of the soil, to its behaviour under cultivation by implements and to the way in which it responds to the sudden dictates of the weather. The scientist has here been able to add precision to the farmer's description and in doing so he has learnt so much of importance about soil texture that we shall devote a whole chapter to his findings (Chapter X).

In this chapter we are concerned, firstly, with the chemical character of the mineral soil colloids, secondly, with their general colloidal behaviour.

**Colloidal Minerals in Soil.**—There would seem, at first sight, no reason why every mineral occurring in rocks should not be found somewhere present as particles of colloidal size. Yet a glance at any textbook of mineralogy will be sufficient to convince one that colloidal minerals are comparatively few in number. In the mineral realm, it appears that the tendency to form crystals is dominant and that in most cases these are able to grow sufficiently to escape the colloidal region altogether. We have only recently learned why this is so. The tendency of most minerals to form crystals is actually due to the strongly geometrical inclinations of the oxygen atoms, which strive whenever they can to pack themselves in orderly arrangement like apples in a box. The other atoms, which in the chemical formulæ appear so much more important than the oxygen, are left with two alternatives. If they are sufficiently small, then they are tucked away in the crevices amongst the oxygen atoms; if they are too large for this, then they compel the oxygen atoms to assume some other orderly arrangement in which they can find a place. Thus oxygen dominates the mineral world in a more subtle fashion than carbon the organic world.

The colloidal minerals of soils fall into three classes: the hydrated oxides, the phosphates and the clays. We know little as yet about the occurrence of the hydrated oxides and the phosphates in soils and it is only in recent years that the clay minerals have begun to be identified with any precision.

### The Hydrated Oxides.

(*a*) *Silicic Acid.* The occurrence of jelly-like masses of silicic acid has from time to time been reported by geologists. These range from soft gels like those prepared in the laboratory from sodium silicate and hydrochloric acid, to hard masses such as agate. They are all non-crystalline and consist chemically of silica ($SiO_2$) with water and small amounts of other oxides. Their colloidal properties agree with those of the chemically prepared gels. It is often assumed that silicic acid gel is present in soils, although there is no direct evidence of this. Very finely divided quartz is probably more common. The fact that treatment of many soils with sodium hydroxide brings silica into solution as sodium silicate does not really prove that silicic acid is present in the original soil.

(*b*) *Ferric Hydroxide.* $Fe(OH)_3$. The yellow, brown or red colour of many soils suggests immediately the presence of ferric hydroxide. It is often found in the coarser fractions of soils as small nodules or concretions. These are made up of aggregates of very small crystals often held together with other brown material which cannot be recognized as crystalline. This brown material is frequently found in the silt and clay fractions and is generally assumed to be ferric hydroxide. However, there are other iron minerals which have a similar colour and which are also colloidal, so that it is difficult to be dogmatic about the occurrence of free ferric hydroxide. In certain tropical soils there is little doubt of its presence in quantity. It is certainly a more common constituent of soils than silicic acid. When colloidal ferric hydroxide is prepared in the laboratory it forms a reddish-brown sol with very small particles. These carry a positive charge which is balanced by mobile negative ions such as chlorine in the liquid. Being positively charged the particles readily flocculate with negatively charged particles of any kind which they encounter. The ferric hydroxide gel is non-elastic and when once dried cannot readily be transformed into the sol. On long standing, sols of ferric hydroxide have been known to deposit crystals. There is evidence that the colloidal particles are plate shaped.

(*c*) *Aluminium Hydroxide.* $Al(OH)_3$. It is often assumed that aluminium and iron hydroxides always occur together in soils. Actually, however, there is less evidence for the occurrence of aluminium hydroxide than for that of iron hydroxide in the soils of the temperate regions. Tropical soils which contain ferric hydroxide generally contain aluminium hydroxide as well, but whereas the ferric hydroxide is seldom crystalline, the bulk of the aluminium hydroxide can be recognized in microscopic crystals known as Gibbsite. The colloidal properties of aluminium hydroxide are very similar to those of ferric hydroxide. The particles normally carry a positive charge, but they can also be negatively charged, and except for being colourless, closely resemble those of ferric hydroxide.

(*d*) *Other Hydrated Oxides.* There is little direct evidence of the occurrence of other insoluble hydroxides in soils.

**The Phosphates.**—In view of the importance of the phosphates in plant nutrition it might be expected that some exact knowledge of their mode of occurrence in soils would have accumulated during their eighty years of ever-widening use as fertilizers. It is not so. The agriculturist has determined the response to phosphatic manures of every conceivable crop on every type of soil. He has encouraged the chemists in the invention of a multiplicity of empirical methods for the detection of phosphate deficiency in soils. And now from a prodigious mountain of literature one may cull only a few crude surmises, a mere thimbleful of facts which approach the heart of the matter.

It is known that phosphates, besides being occasionally present as small crystals of apatite ($Ca_3(PO_4)_2\,CaF_2$), etc., in the sand fraction of soils and possibly also in the silt, are regular constituents of the clay fraction. Here the mode of combination of the phosphorus is completely obscure. It is often assumed that colloidal phosphates of iron and aluminium are present, because in the laboratory soluble iron and aluminium compounds react with phosphates to give such colloidal precipitates. The view has also been widely held that the phosphate ion ($PO_4^{---}$) is held by adsorption at the surface of the above mentioned colloidal hydroxides; a mechanism which again is readily demonstrated on pure materials in the laboratory.

**The Clay Minerals.**—Before embarking on a description of the other and more important colloidal minerals known as the clays we must briefly consider the various uses of the word clay. Thus a farmer frequently refers to a whole soil as a clay, meaning that it is heavy to work, sticky in wet weather and lumpy in dry weather. A brickmaker would only describe as a clay a subsoil which could be baked to form bricks. A potter uses a more restricted definition corresponding to the finer material with which he works, the small stones and gravel having been carefully removed. The soil chemist has adopted a still more restricted definition, confined to a particular fraction of the soil, namely, that containing all the inorganic particles less than $2\,\mu$. Finally, the mineralogist uses the word clay to denote a certain group of minerals containing oxygen, silicon and aluminium or iron as the major constituents. There is no restriction as to particle size. In dealing with the clay minerals we shall adopt this last convention, and when we wish to use the term in the soil chemists' sense we shall write "clay fraction." The clay minerals are at present a somewhat ill-defined group and we can only indicate a few members which have been fairly clearly characterized. Probably many others await discovery.

All the clays belong to an important mineral class whose geometrical structure is built up by the arrangement of the atoms in endless sheets. The micas, the chlorites, talc and gibbsite are other important members. In the clays themselves these sheets are of two kinds. The silica sheet has the composition $Si_2O_3(OH)_2$. The alumina sheet has the composition $Al_2(OH)_6$. In the kaolin group the molecule may be constructed by laying a silica sheet over an alumina sheet. Once in the correct position the two sheets adhere chemically because certain of the oxygen atoms act as links between them whilst others are eliminated as water along with part of the hydrogen. Thus we may have :

$$Si_2O_3(OH)_2 + Al_2(OH)_6 = Si_2O_3.Al_2O_2(OH)_4 + 2H_2O$$

(Kaolinite).

or

$$Si_2O_3(OH)_2 + Al_2(OH)_6 = Si_2O_3.Al_2O(OH)_6 + H_2O$$

(Halloysite).

The complete crystals are simply piles of these double sheets. In the montmorillonite group (see below) the molecule probably consists of three sheets—two silica and one alumina.

(*a*) *The Kaolin Group.* Two members are found in soils, kaolinite and halloysite. The former constitutes the china clay of the potter. Comparatively speaking, it has a high tendency towards crystallization and particles less than 100 m$\mu$ are rarely encountered. Halloysite is the most highly colloidal mineral of this group. The colloidal particles of these clays are negatively charged in water, the negative charge being balanced by ions like sodium, calcium and hydrogen in the liquid. Cation or base exchange can therefore occur with solutions of salts, acids or bases. It is restricted, however, to the outer surface of the particles and since the degree of dispersion is comparatively low the exchange capacity per gramme of clay is only moderate, even with halloysite.

(*b*) *The Montmorillonite Group.* In this important group of the clays there are several peculiarities of structure which, in view of their widespread occurrence in soils, are worthy of close consideration. As already mentioned, three layers, two silica and one alumina, are closely bound together to form the molecule, constituting a triple sheet. These molecular sheets are much less firmly held together than the double molecular sheets of the kaolin group. In fact, water molecules are able to penetrate between them and so to increase their distance apart to about $1 \cdot 5$ m$\mu$. This process does not lead to complete disruption, but it so weakens the structure that very slight mechanical forces can do so and can cause a great increase in the degree of dispersion. The colloidal character of these clay minerals is thus very fully developed and particles less than 50 m$\mu$ are of frequent occurrence.

These clays differ from those of the kaolin group in another important respect. The sheets are seldom of the ideal composition. The structure of the $Al_2(OH)_6$ layer is such that three atoms of magnesium can replace two of aluminium without much distortion. Similarly, one atom of iron can replace one atom of aluminium. In the $Si_2O_3(OH)_2$ layers an atom of aluminium can replace one of silicon, but in order to make the valencies still balance ($Si = 4$ and $Al = 3$) one atom of sodium or potassium or half an atom of calcium or magnesium must be incorporated at the same time as the aluminium. But in the complete structure these cations can only find places either between the silica and alumina layers or else in the larger spaces between the complete sheets. Hence a high proportion of these cations are readily displaced and they constitute in actual fact, the major portion of the exchangeable bases. In the clays of this group, therefore, the exchangeable bases are of two kinds—those belonging to the outer surfaces of the particles, and those resident inside them. There is no means of clearly distinguishing between the two categories, but there is strong evidence that in most cases 80 per cent. or more of the base exchange is internal.

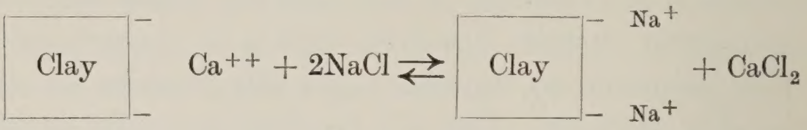
The older formulæ for the minerals of this group are misleading. *Beidellite* (formerly $Al_2O_3$. $3SiO_2$. $3H_2O$) is the member whose predominating replacement is that of Al + cations for Si. At the same time Fe may replace Al and when this latter effect has led to the formation of a complete layer $Fe_2(OH)_6$ in place of $Al_2(OH)_6$ the mineral is given the name *Nontronite.* In *Montmorillonite* (older formula MgO. $Al_2O_3$. $5SiO_2$. $nH_2O$) magnesium partially replaces aluminium and at the same time there is often a small replacement of Al + cations for Si and of Fe for Al.

So far as our present knowledge goes, beidellite and montmorillonite are much commoner than nontronite in soils of the humid regions. They are highly colloidal and the particles carry a negative charge in water. The base exchange capacity is high.

The finest material of a soil consists in most cases of a mixture of clay minerals, sometimes one and sometimes another of them predominating. But we know, as yet, very little about the details of the occurrence of these clay minerals. Their identification is difficult and for the most part the chemists' studies have been carried out with the clay fraction as it stands, if not with the whole soil. We are reasonably certain, however, that it is exceptional for the clay minerals to dominate the silt fraction as they do the clay fraction. The silt fraction generally consists of fragments of the usual rock-forming minerals, amongst which the felspars often predominate.

We have already mentioned the varying capacities of different clay minerals for undergoing the base exchange reaction, and we must now consider this reaction in detail as it is, next to photosynthesis, the most important chemical reaction in the whole demain of agriculture.

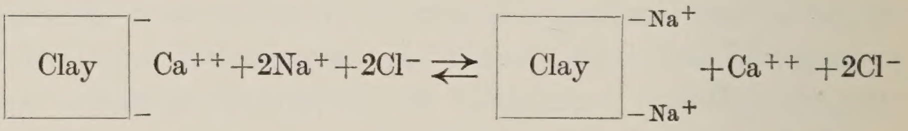
**Base Exchange.**—The nature of the reaction which we term base exchange is already familiar as a general property of the outer, mobile ions attached to negatively charged colloidal particles. In describing kaolinite we have also noted its potentialities as a surface reaction in soils. But beidellite and montmorillonite far transcend kaolinite in the number of cations which for a given weight of material can take part in this change ; comparing, of course, particles of the same size. We infer, therefore, that in these clays part of the base exchange process occurs inside the colloidal particle in fine pores, cracks or capillaries which are filled with water molecules. Since the colloidal particles themselves may be quite small these internal pores must be very minute indeed. We cannot see them, even with the best ultramicroscope, and we can only infer their presence indirectly. Further, we have as yet no means of distinguishing the reactions which go on inside these pores from those which occur on the outer surface of the clay particles. We therefore represent base exchange reactions by some non-committal, diagrammatic equation such as the following :



$$\boxed{\text{Clay}}\begin{matrix}-\\ \\ -\end{matrix}\quad \mathrm{Ca^{++}} + 2\mathrm{NaCl} \rightleftarrows \boxed{\text{Clay}}\begin{matrix}-\ \mathrm{Na^{+}}\\ \\ -\ \mathrm{Na^{+}}\end{matrix} + \mathrm{CaCl_2}$$

In spite of our ignorance of the detailed mechanism of base exchange we have acquired much useful information about its general character, which may be summarized as follows :

(1) The reaction is so quick as to appear instantaneous. This fact is very significant to the chemist. It means that the reaction occurs between charged ions, not between electrically neutral molecules. It is more correct therefore to write the equation we have just given in the form :



$$\boxed{\text{Clay}}\begin{matrix}-\\ \\ -\end{matrix}\quad \mathrm{Ca^{++}} + 2\mathrm{Na^{+}} + 2\mathrm{Cl^{-}} \rightleftarrows \boxed{\text{Clay}}\begin{matrix}-\mathrm{Na^{+}}\\ \\ -\mathrm{Na^{+}}\end{matrix} + \mathrm{Ca^{++}} + 2\mathrm{Cl^{-}}$$

which shows clearly that the reaction is between the cations only.

(2) The reaction is always reversible. In the example just given, no sooner have the sodium ions attached themselves to the clay and the calcium ions replaced them in the outer solution than these also begin to react with one another giving clay saturated with calcium ions and sodium ions in solution. The speeds of the forward and the reverse reactions are generally different so that the mixed system which results is seldom a fifty-fifty one. If, however, we wish the reaction to proceed to a finish in any particular case we can always force it by removing the soluble product as quickly as possible and treating the clay or soil with more of the original solution. In

this way we continually reduce the concentration of the original ion and hence the effectiveness of the reverse reaction, until finally the latter ceases. Starting, for instance, with a clay associated only with calcium ions, we could prepare the corresponding clay associated only with sodium ions by washing continuously with fresh sodium chloride solution. It is this kind of continuous washing or leaching which is so important in soil formation processes, as we shall see later.

(3) We must now consider the effectiveness of the various cations as displacing agents in base exchange reactions. We can easily compare them by finding the amount of exchange which occurs when the two cations concerned are present in equal numbers. Such figures, expressed as percentages of the total exchange capacity of the clay, are known as *symmetry values.* Table II gives symmetry values for a clay consisting chiefly of beidellite, on treatment with solutions of various salts.

TABLE II

SYMMETRY VALUES FOR PUTNAM CLAY

| | | | | | | |
|---|---|---|---|---|---|---|
| Clay ion . . | $NH_4$ | $NH_4$ | $NH_4$ | Na | Na | $NH_4$ |
| Ion added . . | Li | Na | K | K | Ca | H |
| Hydration . . | 27 | 18 | 12 | 12 | 28 | 1–10 |
| Symmetry value . | 32 | 33 | 64 | 60 | 76 | 93 |

It is interesting to note that the order of effectiveness of the various cations is the same as is normally found for the coagulation of negatively charged colloids. The divalent cations are more effective than the monovalent ones, and for ions of the same valency the effectiveness increases as the hydration of the cations entering decreases. (The hydration figures in Table II are expressed as molecules of water per ion.) Thus we see that potassium enters by exchange more readily than sodium, calcium more readily than potassium and so on. There is one exception to the rule that monovalent ions are less effective than divalent ones. The hydrogen ion far transcends other monovalent ions and is comparable with calcium and barium in its power of replacement. It will be remembered that its coagulating power for negatively charged colloids was also unusually high and we may ascribe all these peculiarities to its minute size and simple structure.

But base exchange, unlike simple adsorption, involves the displacement of ions originally present, and the symmetry value obtained in any given case will depend as much on the original ions present in the clay as on those added in solution. It is found that, with very few exceptions, the ions which enter the clay most readily are the most difficult to replace subsequently. Thus if in Table II the symmetry values for a calcium clay had been given, they would all have been lower than those for the sodium clay. One cation of common occurrence is exceptional. The magnesium ion is more strongly hydrated than calcium and gives a lower symmetry value when it enters a clay, but once it has entered, it becomes more difficult to displace.

We see, therefore, that in base exchange any cation may be taken up by a soil and that, once held, it may subsequently be displaced by any other cation. The persistence or retention of a cation depends both on the extent to which it is taken up and on the likelihood of its displacement later. These conclusions are of importance in two respects. They enable us to give a logical explanation of many processes of soil formation (see Chapter IX) and also to predict the consequences arising from the application of fertilizers.

In order to form some concrete idea of the magnitude of the changes which can be brought about by use of fertilizers we require information both on the capacity of soils for base exchange and on the cations already present. In Table III figures are presented for fertile, arable soils which would be described as light loams and heavy loams in character. Neither contains much humus, which as we shall see later, has itself a very high capacity for base exchange.

TABLE III

| Soil. | % Clay Fraction. | Crop. | Plot. | Year. | Exchangeable Cations. (M. Eq. per 100 grm.) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Ca | Mg | Na | K | H |
| Woburn (sand) | 10 | Barley | Unmanured | 1876 | 9·23 | — | — | — | — |
| ,, | ,, | ,, | ,, | 1888 | 6·85 | 1·06 | 0·47 | 0·25 | — |
| ,, | ,, | ,, | ,, | 1927 | 3·76 | 0·67 | 0·26 | 0·17 | 5·04 |
| ,, | ,, | ,, | $NaNO_3$ | 1927 | 4·95 | 0·58 | 0·34 | 0·16 | 5·17 |
| ,, | ,, | ,, | $(NH_4)_2SO_4$ | 1927 | 1·16 | 0·58 | 0·30 | 0·19 | 7·77 |
| Rothamsted (Heavy Loam) | 15 | Wheat | Unmanured | 1923 | 13·57 | 0·75 | — | 0·42 | — |
| ,, | ,, | ,, | $(NH_4)_2SO_4$ | 1923 | 13·60 | 0·70 | — | 0·30 | — |

The significance of these figures becomes clearer to the agriculturist when the figures for base exchange capacity are translated into the more familiar guise of tons per acre, adopting the usual convention of 1,000 tons of surface soil per acre. The Woburn sand, for instance, had in 1888 1·37 tons of calcium (equivalent to 1·92 tons of lime), 0·129 tons of magnesium, 0·108 tons of sodium and 0·098 tons of potassium in the exchangeable form per acre. In both soils the calcium predominates over the other cations, a state of affairs which is typical of fertile soils almost everywhere.

What happens when fertilizers are applied to these soils ? Let us take nitrate of soda as a simple example. As soon as this salt dissolves in the soil water it immediately reacts with the clay in each of the following ways :

$$\boxed{\text{Clay}}^{-}_{-}\ \text{Ca}^{++}+2\text{Na}^{+}+2\text{NO}_3^{-} \rightleftarrows \boxed{\text{Clay}}^{-}_{-}\ 2\text{Na}^{+}+\text{Ca}^{++}+2\text{NO}_3^{-}$$

$$\boxed{\text{Clay}}^{-}_{-}\ \text{Mg}^{++}+2\text{Na}^{+}+2\text{NO}_3^{-} \rightleftarrows \boxed{\text{Clay}}^{-}_{-}\ 2\text{Na}^{+}+\text{Mg}^{++}+2\text{NO}_3^{-}$$

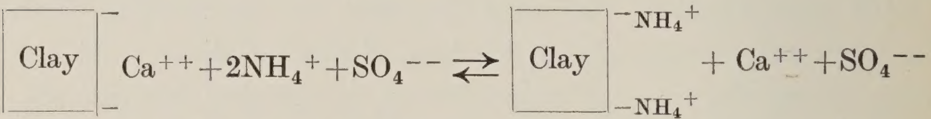
$$\boxed{\text{Clay}}^{-}\ \text{K}^{+} + \text{Na}^{+} + \text{NO}_3^{-} \rightleftarrows \boxed{\text{Clay}}^{-}\ \text{Na}^{+} + \text{K}^{+} + \text{NO}_3^{-}$$

Since, however, the calcium clay is present in greatest amount the first of these reactions greatly predominates. Indeed, the second and third are not always recognized in field experiments although there is no difficulty in demonstrating their presence in the laboratory. Thus in the Woburn experiments on the continuous manuring of barley, the nitrate of soda plots contained the following amounts of exchangeable bases in 1927 : calcium 0·99 tons ; magnesium 0·070 tons ; sodium 0·078 tons ; potassium 0·062 tons. Now over the whole period of fifty years 1·2 tons of sodium per acre had been applied. Comparing these figures with those given above, which refer to the unmanured plot in 1888 (complete figures for 1876 are unfortunately not available), the small losses of magnesium and potassium are noteworthy, but even more remarkable is the slight decrease in the sodium. The above equations would lead us to expect an increase in the sodium. In other experiments, such as those at Rothamsted, this increase has been clearly demonstrated.

Discrepancies of this kind between the base exchange equation and the results in the field are not infrequent.

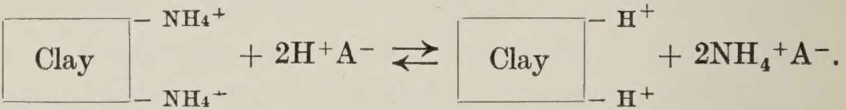
It must be remembered that the base exchange equation represents an equilibrium instantaneously set up between soil and solution. In the field this initial equilibrium is not maintained. It is modified by a whole series of factors. A shower of rain causes the soil water to move downwards, away from the clay with which it was in equilibrium and into a new environment. The clay, formerly in contact with this solution, has now to come to equilibrium with a fresh one containing much less of the fertilizer. At the same time the original soil solution, in moving downwards, has come into contact with fresh clay with which it also attains a different equilibrium. Further, the presence of a growing crop alters the initial state, since plants take up cations in proportions generally different from those of the soil solution at equilibrium. Finally, soils contain reserves of cations apart from those present in the exchangeable form. These reserves of calcium, magnesium, sodium and potassium are found to some extent in the clay minerals themselves, but they are probably more readily liberated from common rock-forming minerals such as calcite, dolomite, the felspars, the pyroxenes and the amphiboles. Even under the influence of pure water, but more markedly under that of the slightly acid soil water containing carbon dioxide, these minerals undergo a slow decomposition. In the case of calcium carbonate an equilibrium is very rapidly established and notable amounts of calcium come into solution as the bicarbonate, according to the equation. $CaCO_3 + H_2CO_3 = Ca(HCO_3)_2$. Thus calcium is enabled to dominate the soil solution, and so long as this obtains, the addition of fertilizers will have no permanent effect on the exchangeable bases in the clay. The liberation of calcium, sodium and potassium from the felspars is a much slower process, insufficient to mask the direct effect of fertilizers on the exchange cations of the clay yet probably adequate to prevent the cations of the fertilizer from entirely displacing those originally present.

We may now study the more complex changes which occur when sulphate of ammonia is used as a fertilizer. The initial reaction consists in the replacement of exchangeable calcium by the ammonium ion thus :



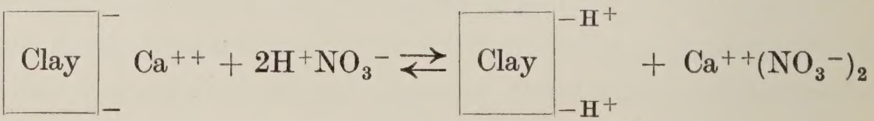
$$\boxed{\text{Clay}}\begin{array}{l}-\\ \\ -\end{array} Ca^{++}+2NH_4^{+}+SO_4^{--} \rightleftarrows \boxed{\text{Clay}}\begin{array}{l}-NH_4^{+}\\ \\ -NH_4^{+}\end{array} + Ca^{++}+SO_4^{--}$$

Calcium is liberated and passes into the soil solution, being eventually lost in the drainage water, along with the sulphate ion. Two things may now happen. Growing plants may take up the ammonia ions directly from the clay, in which case the acids produced by the roots react with it as follows :



$$\boxed{\text{Clay}}\begin{array}{l}-NH_4^{+}\\ \\ -NH_4^{+}\end{array} + 2H^{+}A^{-} \rightleftarrows \boxed{\text{Clay}}\begin{array}{l}-H^{+}\\ \\ -H^{+}\end{array} + 2NH_4^{+}A^{-}.$$

In this equation A represents the anion of any organic acid likely to be present. A hydrogen clay, or clay acid has thus been produced, the hydrogen ions produced being equivalent to the ammonium ions originally applied. Instead of its being absorbed directly by plants, the nitrifying organisms may act on the ammonium salt liberated according to the above equation, giving one molecule of nitric acid for each molecule of ammonia. Now such acid will react readily and very completely with more of the original clay, since the hydrogen ion has a very great power of replacement.



$$\boxed{\text{Clay}}\begin{array}{l}-\\ \\ -\end{array} Ca^{++} + 2H^{+}NO_3^{-} \rightleftarrows \boxed{\text{Clay}}\begin{array}{l}-H^{+}\\ \\ -H^{+}\end{array} + Ca^{++}(NO_3^{-})_2$$

Once again, a soluble calcium compound has been produced and a hydrogen clay remains. Growing plants may now take up this nitrate. We see, therefore, that for each molecule of sulphate of ammonia applied, one or two atoms of calcium can be lost according to the fate of the nitrogen. We might expect 1 cwt. of sulphate of ammonia, on this basis, to cause the loss of 0·475 and 0·95 cwt. of lime respectively. Actually in the Woburn experiment the extra loss of lime over that of the control plot caused by the application of 3·49 tons sulphate of ammonia over fifty years was only 0·73 tons; that is, at the rate of 0·21 cwt. lime per cwt. of fertilizer. Once again, it is clear that the base exchange equations whilst indicating the general trend, cannot be used accurately to foretell the changes caused by fertilizers.

It is clear, also, that of the two soils whose base exchange properties are summarized in Table III the Rothamsted soil has withstood the exchangeable base depletion caused by the continued use of sulphate of ammonia remarkably well. There is no difference in exchangeable calcium between the unmanured plot and that which has had sulphate of ammonia for eighty years. Evidently reserves of calcium are present which continually make good the losses. As might be expected, these reserves are present in the form of calcium carbonate. In this case the action of the fertilizer is only shown by the drainage water which carries away calcium equivalent to 800 lb. of calcium carbonate per acre from the unmanured plot and to 1,100 lb. from the sulphate of ammonia plot.

These concrete examples of the effects of base exchange are only two of many. In the absence of fertilizers cations are, under humid climates, continually being liberated from the clays by exchange for hydrogen ions. These last are ubiquitous. Rainwater itself is slightly acid and it is liable to become more so in the soil, whose teeming microbial life provides abundant carbon dioxide. The higher plants themselves are able to promote this same replacement of other cations by hydrogen, since their roots furnish organic acids which come into direct contact with the soil. Cations are thus made available, which would otherwise remain attached to the clay. The base exchange reaction, therefore, is largely instrumental in providing the root cells with some of those mineral constituents which are absolutely essential to life. It provides the first link in the chain of chemical reactions which lead from the soil to the mature crop.

The base exchange reaction has been described before the other properties of the clays for two reasons. The great intensity in clays like beidellite and montmorillonite proves that it is not merely a reaction at the outer surface such as we have already discussed as a general property of negatively charged colloids. Yet this intensity is less than that found in the other important soil colloid—the humus. Both classes of soil colloids are therefore more reactive than their external surfaces would indicate. In the clays it is probable that the internal cations are held, not irregularly, as in the cavities of a sponge, but in minute channels having a definite place in the crystal architecture of these minerals. On the other hand, in humus no crystalline character is apparent and all the cations are replaceable. This leads us to conclude that molecules present can be reached by cations from the surrounding liquid, which accords well with the high water content of the humus gels.

**The Colloidal Properties of the Clays.**—We must now examine the surface properties which have been described for colloidal systems in general in Chapter V. The electrical double layer first claims attention. The way in which the speed of a clay particle under an electric field varies with the exchangeable cation is shown in Table IV. Here the determinations were made on the clays in contact with pure water. The differences do not, at first sight, suggest great variation in the stability and character of the dilute suspensions. It must be remembered, however, that coagulation, which is one of the most fundamental changes a colloidal system can undergo, is generally initiated long before the potential of the double layer and the cataphoretic velocity are reduced to zero. In column 5 are given the actual velocities for which slow coagulation sets in.

## TABLE IV

### Cataphoresis and the Exchangeable Cations of a Clay

| Clay. | Type. | Cation. | Cataphoretic Velocity (in $\mu$ per sec. for 1 volt per cm.). | Critical Velocity. |
|---|---|---|---|---|
| Putnam | Beidellite | H | 2·70 | 2·7 |
| | | Li | 3·53 | 3·0 |
| | | Na | 3·57 | 2·9 |
| | | K | 3·47 | 2·7 |
| | | Ca | 2·11 | 2·1 |
| | | Mg | 2·32 | 2·3 |

From these figures one would conclude that the hydrogen, calcium and magnesium clays are unstable in the dispersed condition since the measured velocity of cataphoresis is practically the same as that for which coagulation begins. Actually these clays form stable suspensions only at low concentrations and coagulate spontaneously at high concentrations. In the case of the lithium, sodium and potassium clays no coagulation is possible until sufficient salt has been added to lower the velocity by 0·5–0·7 $\mu$ per second. It may be concluded, therefore, that in the field the hydrogen, calcium and magnesium clays will always be in a coagulated state. They cannot readily be dispersed even when abundant water is present. Sodium clays, which also occur naturally (see Chapter IX), very readily pass into a completely dispersed condition as soon as the rainfall is sufficient to bring the concentration of salts in the soil water below that required for coagulation.

Many experimental studies have been made of the influence of salts, acids and bases on the coagulation of the clays. In the earlier experiments the effect of the exchangeable cation on coagulation was not fully appreciated. Its importance will be clear from Table V, in which the figures represent the percentage diminution in the original number of clay particles caused by coagulation for 30 minutes.

TABLE V

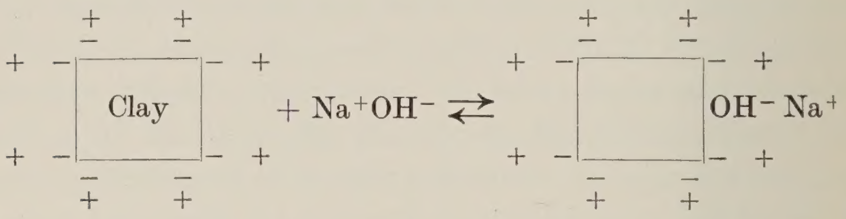
THE COAGULATION OF Na, K, AND Ca CLAYS BY KCl AND $CaCl_2$

| Salt. | Concentration. | Na Clay. | K Clay. | Ca Clay. |
|---|---|---|---|---|
| KCl | 0·001 N | 6·6 | 8·6 | 32·4 |
| ,, | 0·010 N | 29·4 | 34·2 | 67·3 |
| ,, | 0·100 N | 65·6 | 67·7 | 78·8 |
| ,, | 1·000 N | 72·9 | 74·5 | 78·8 |
| $CaCl_2$ | 0·001 N | 12·6 | 13·2 | 39·3 |
| ,, | 0·010 N | 58·2 | 67·1 | 83·3 |
| ,, | 0·100 N | 74·9 | 79·0 | 83·3 |
| ,, | 1·000 N | 74·9 | 79·0 | 83·3 |

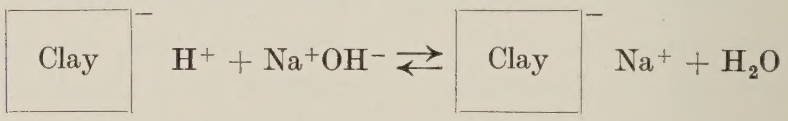
Throughout this series of experiments the calcium clay coagulates more rapidly than the sodium and potassium clays. For the highest concentrations of salts the difference is small; obviously because the clays are here in the region of quick coagulation where the speed depends only on the initial number of particles (see p. 23). In the 0·001 N solutions the calcium clay coagulates much more rapidly than the sodium and potassium clays. Comparing now the two salt solutions at the same concentration it is clear from these figures that calcium chloride is more effective than potassium chloride. For the clays in general it may be said that the order of effectiveness of different salts as coagulators follows the series $Na < K < Mg < Ca < H$, which is the usual order for negatively charged systems. The exact concentrations of salts which would be needed to cause coagulation of clays under field conditions cannot be found by experiments such as those discussed above. Concentrated clay systems are much more sensitive to coagulating agents than dilute ones, and it is only in the most dilute suspensions that quantitative experiments can be carried out.

The great effectiveness of acids as coagulating agents is analogous to their action on other negatively charged colloids. We have already noted that the hydrogen ion very readily displaces other exchangeable ions, even calcium, from the clay. In most instances, therefore, where clays are flocculated by acids a very considerable proportion of the exchangeable bases originally present will be displaced.

Coagulation by bases has proved a more puzzling phenomenon in the study of the clays than the action of salts and acids. The hydroxyl ion, as we have noted in Chapter V, has a remarkable power of penetrating the ionic atmosphere surrounding colloidal particles and of attaching itself firmly by adsorption at the surface. Thus in small concentrations the effect of a base is to increase the negative charge on the particles and so to diminish their sensitivity towards coagulating agents. At higher concentrations the normal effect of the cation comes into play and flocculation eventually occurs. Because of this stabilizing effect of the hydroxyl ion the critical concentration for a base is appreciably higher than that for salts having the same cation. Diagrammatically we can represent the action thus :



The stabilizing action of bases is also manifested in another way. If the external cation of the colloidal particle is hydrogen, then the first action of a base is purely chemical, the hydrogen ions combining with the hydroxyl ions of the base to form water. The cation of the base then becomes the external cation of the colloidal particle. For a hydrogen clay we have, for instance :



Now, as we have seen, a hydrogen clay is much more sensitive to coagulating agents than a sodium clay. The production of a sodium clay thus enhances the stability. This action will obviously only be appreciable for cations like sodium, potassium and ammonium. Calcium and magnesium clays produced in this way are just as sensitive to coagulating agents as the original hydrogen clay.

However, in spite of these two stabilizing mechanisms it is frequently found that calcium hydroxide is a better coagulating agent than any calcium salt. The phenomenon is not confined to the clays. It has been reported for silicic acid, for ignited quartz and for permutite suspensions. Nor is calcium hydroxide the only substance showing this effect. Mixtures of calcium salts with sodium hydroxide also show it, and, more plainly still, mixtures of magnesium salts with sodium hydroxide. In fact, the salt of almost any metal which forms a sparingly soluble hydroxide shows an enhanced coagulating action in presence of sodium hydroxide. The most curious feature of this type of coagulation is that it occurs for abnormally high values of the cataphoretic velocity. The presence of the base raises the speed of migration in an electric field ; yet in spite of this an accelerated coagulation results. Various explanations of these unusual effects have been brought forward. None is wholly satisfactory. It is certain, however, that the formation of positively charged insoluble metal hydroxides in a negatively charged clay suspension does cause abnormally rapid coagulation. This was to be expected since positive and negative particles can attract one another. What still remains obscure is the increase in the cataphoretic velocity of the clay.

One other curious discrepancy in the results of flocculation experiments is of importance. It is found that the abnormally potent coagulating action of calcium hydroxide is not shown by the silt fraction as it is by the clay fraction. This fact was formerly regarded as evidence in favour of the view that clay particles are built up of a “ suspensoid ” core with the normal coagulating properties of the silt fraction and an " emulsoid " coating which displays the abnormal behaviour with calcium hydroxide. We know, however, from studies of the protective action (see Chapter VI) that when a particle is coated with a gelatinous colloid it then acquires the complete colloidal properties of the coating. The difference in coagulating properties between the silt and the clay is more simply ascribed to their marked mineralogical and chemical differences. Clay particles when completely dispersed are now regarded as being homogeneous.

The conception of the " emulsoid " coating is, however, extraordinarily useful when we come to consider coagulated or flocculated systems, such as the soil itself; for here it rests on a firm physical basis. We have already noted in Chapter V that in the coagulation of polydisperse systems the chief tendency is for the finest particles to unite with the larger ones. In this way the coarsest clay particles and the silt particles can acquire a gelatinous coating of the finest clay which will remain so long as the system is flocculated. When, however, peptization is caused, as in the preparation of a soil for mechanical analysis, the association is completely destroyed and particles of every size behave as separate entities.

**Clays as Gels.**—The study of coagulation leads us naturally from the dilute suspension to the more concentrated system until finally we arrive at the gel, in which the union between particle and particle has proceeded so extensively in space that a solid results. A gel need not have all the mechanical properties of a solid to the exclusion of all those of a liquid. In most instances of gel formation a comparatively large amount of liquid is enmeshed amongst the colloidal particles. Four factors are concerned in the formation and the properties of every gel. They are: (1) the ratio between the total volume of the colloidal particles and the volume of free liquid between them; (2) the amount of liquid firmly held in the interior and at the surface of the colloidal particles, (3) the strength of the union between the colloidal particles; (4) the arrangement or architecture of the colloidal particles throughout the gel. The fact that the study of gels has been qualitative rather than quantitative is chiefly due to the interplay of these factors. Thus it is impossible to change (1) or (2) without affecting (3) or (4) and indeed we have not even succeeded in defining (1) and (2) satisfactorily since they merge imperceptibly into one another (see Chapter VI). The technical importance of the clays has, however, encouraged their study, albeit along somewhat empirical lines.

We may deal first with the intermediate state of the clays in which the character is that of a paste, neither truly liquid nor truly solid. Passing from dilute suspensions through systems of increasing concentration, the first solid property to become apparent is that of elasticity. Even at concentrations as low as 2–10 per cent. it is often found that after rotation of the system in a cylindrical vessel it first comes to rest and then moves backwards over a short distance. A true liquid would, of course, remain stationary after once coming to rest. As the concentration is raised a more pronounced manifestation of the same character sometimes appears. The clay-water system is then solid when stationary, but flows like a liquid when shaken, reverting back to the solid some time after coming to rest (thixotropy). These effects have so far received little study as regards clays in general, the work having been confined almost entirely to bentonite. It has been shown that both of these effects are consequent, at low concentrations, on slow coagulation which leads to a spreading network of loosely linked aggregates. A slight mechanical force is sufficient to rupture this system, but it re-forms readily when movement ceases.

As the concentration of clay is raised another solid property appears, that of *plasticity*. By this we mean, in general terms, the permanent modification of the shape of a solid by pressure. All the substances which can be moulded or modelled into shape by hand have this property. The clays possess it in a marked degree ; hence plasticity lies at the basis of the potter's craft. Unfortunately, its scientific definition and its measurement in physical units are extraordinarily difficult. It has been shown by experiments on the behaviour of clay pastes in capillary tubes that plasticity is probably an amalgam of two physical properties. One is known as the static rigidity and may be regarded roughly as the force required to overcome the internal linkages so that the non-flowing solid becomes the yielding liquid. The second is a kind of viscocity (pseudo-viscosity) ; that is, it expresses numerically the liquid friction once flow has commenced. Both quantities increase with concentration of the clay, and both are affected by coagulating agents.

Finally, the stage is reached in which the amount of clay is greater than that of the water. The force required for deformation now becomes much greater and the solid properties predominate. In natural soils the clay is generally in this state, which makes the laboratory measurements bear a very close relationship to field behaviour. In this chapter we must confine our attention to the laboratory methods. The connection with soil management and cultivation will be emphasized in Chapter X.

We have learned in Chapter VI that gels may be divided into two main classes, the elastic and the non-elastic, and that the curves connecting the quantity of water in the gel with the vapour pressure are different for the two. The general shape is the same, but whereas the elastic gels show a perfectly reversible behaviour, the non-elastic gels depart markedly from true reversibility. The vapour pressure relationships of the clays have been studied from two aspects. On the agricultural side the chief interest lies in the connection between vapour pressure and water content, since in the field the commonest change is an alternate drying and wetting. From the point of view of the pottery industry, however, the change in vapour pressure or in water content with temperature is of greater interest, because the curves obtained throw light on the chemical changes which clays undergo in the furnace. The complete picture of a clay-water system involves three variable quantities, the amount of water, its vapour pressure and the temperature. The measurements so far obtained concern only pairs of these three variables. Fig. 10 illustrates the types of curve obtained using soils. Results for separated clay fractions are not available, but in the particular examples in Fig. 10 it may be taken that the humus content is small, so that the curves represent chiefly the clay-water—water vapour relationship. Perfect reversibility was found. Towards the top portion of the curves, where the vapour pressure approaches that of pure water the systems were very slow in attaining equilibrium.

Some attention has been paid to the shrinkage of clays on drying, a problem whose agricultural significance is obvious to all who are familiar with the cracked surface of clay land in dry weather. When the volume of a clay block is plotted against its water content a discontinuous curve is obtained (Fig. 11). It consists of three parts. Starting with a moist block it is first found that loss of water and decrease in volume are exactly proportional to one another.

This is represented by the portion AB of the curve. At B the appearance of the block begins to change. It becomes lighter in colour as air enters the larger pores. From B to C, however, a slight further shrinkage occurs (known as *residual shrinkage*), and at the same time air progressively takes the place of water. From C to D there is no further shrinkage and the clay finally attains its normal air-dried condition. The phenomenon of residual shrinkage is not shown by kaolin, but kaolin when coated with silicic acid gel acquires this property. Hence it is inferred

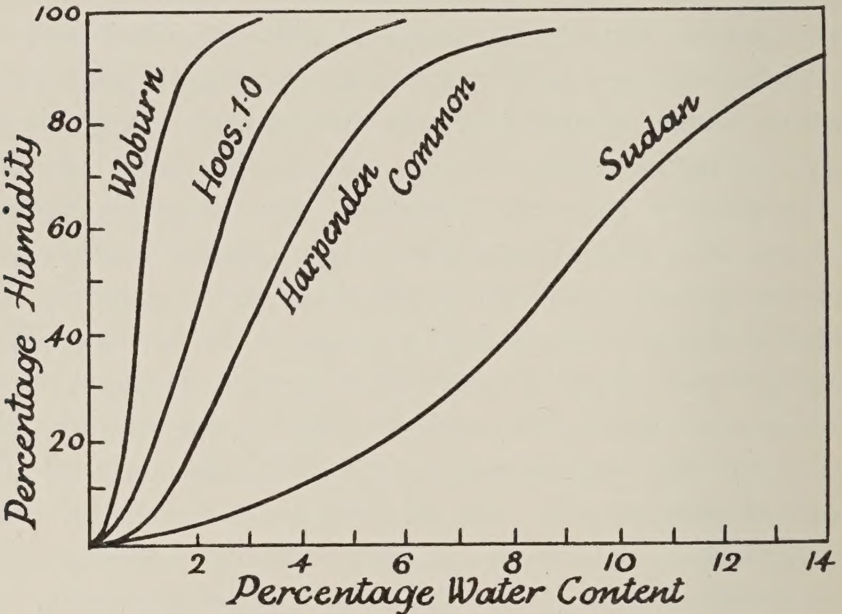


FIG. 10.—Vapour Pressure Curves of Soils.

The Woburn soil has a low and the Sudan soil a high Clay content.

(From the *Journal of Agricultural Science* and B. A. Keen's *The Physical Properties of the Soil.*)

that residual shrinkage is due to the shrinkage on drying of the colloidal coating which surrounds the larger particles. The air is already able to enter the largest pores before the shrinkage of the finest material present is complete. When a block of clay which has been dried in this way is re-wetted it acquires immediately a greater volume than its moisture content for the drying process would indicate. The curve for increasing amounts of water thus lies completely above that for drying. This increased volume is due to a loosening which eventually leads to a disruption of the whole block. The experiment is the laboratory counterpart of the production of a fine tilth on clay soils by dry weather followed by a shower of rain.

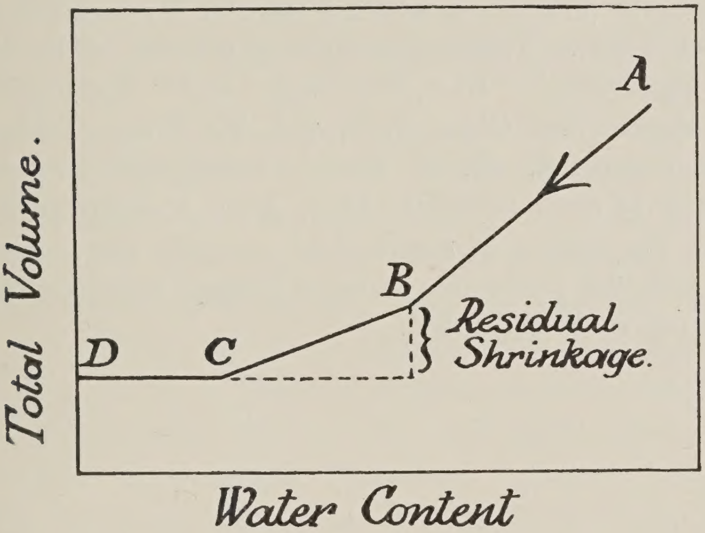


Fig. 11.—The Shrinkage of Clay on Drying.

## Supplementary Reading

The subject of the mineralogy of the clays is at present changing so rapidly that no textbook can be up to date for long. Two older works, F. W. Clark's *The Data of Geo-*

*chemistry* (3rd ed., New York, 1916) and G. W. Merrill's *Rocks, Rock-weathering and Soils* (London, 1906), still retain their importance in considering the weathering of rocks. The following modern books on soils all devote considerable space to base exchange and the colloidal properties of clays: N. M. Comber's *An Introduction to the Scientific Study of the Soil* (2nd ed., London, 1932), E. J. Russell's *Soil Conditions and Plant Growth* (5th ed., London, 1933), G. W. Robinson's *Soils* (London, 1932). Three summarizing articles by G. Wiegner on " Coagulation," " Base Exchange " and " Hydrogen Clay " in the *Journ. Soc. Chem. Ind.*, Vol. 50, Trans. 1931, should also be consulted. B. A. Keen's monograph *The Physical Properties of Soils* (London, 1931) gives a complete development of the theory of mechanical analysis, and a discussion of the colloidal properties of clays largely based on the work carried out at Rothamsted.

# CHAPTER VIII

## THE ORGANIC COLLOIDS OF SOIL

From very early times agriculturist have recognized the importance of humus in the soil. With reiterated emphasis they have described its beneficial action ; its lightening effect on heavy soils, its valuable water-retaining capacity on light soils, its function as a reservoir of plant nutrients. Down to the time of Liebig humus itself was regarded as the chief plant food, and the earlier chemists carried out their investigations with a very full consciousness of its importance. The great Berzelius himself helped to establish two major facts ; firstly, that humus is a mixture, and secondly, that it is chiefly a mixture of organic acids or of salts of these acids. The acceptance of Liebig's views on plants nutrition diverted the attention of agricultural chemists from the study of humus, whilst its colloidal character (first clearly recognized by van Bemmelen in 1888) kept at bay the organic chemists who threw themselves so whole-heartedly into the elucidation of the chemistry of natural products like the sugars, the terpenes and even the proteins during the latter part of the nineteenth century. More recently, the question as to the chemical constitution of the acids of humus has been attempted by fuel chemists. The reason for this development lies in their conviction that humus, as typified by peat, represents the first stage in the formation of coal. Many of their experiments and conclusions are directly applicable to the problem of the constitution of humus in the soil.

**The Complex Nature of Humus.**—The word humus, like the word clay, is used in different senses by different individuals. To most farmers it represents, somewhat vaguely, the sum total of all that organic matter in the soil whose nature is not obvious to the eye. The chemists work with a more restricted definition. They would exclude from consideration all undecomposed plant residues and all micro-organisms. Chemists often use the term "humic matter" rather than "humus" in order to make it clear that they mean only the black colloidal material which accumulates in the soil as a result of the decomposition of plant and animal remains. Humic matter occurs naturally in two forms. In the one it is a mixture of colloidal acids and this form is characteristic of high moor peats and of sour soils generally. In the other it is present as the calcium salts of these acids and this form predominates in fen soils, in calcareous soils and in fertile mineral soils with a neutral or slightly alkaline reaction. Intermediate types are present in soils of slight acidity.

In the chemical fractionation of humic matter the primary separation distinguishes four groups: (1) water-soluble acids which are yellow or brown in colour, the *fulvic acid* fraction; (2) black acids soluble in alcohol but insoluble in water, the *hymatomelanic acid* fraction; (3) black acids, insoluble in alcohol and in water but forming soluble sodium, potassium and ammonium salts, the *humic acid* fraction; (4) black acidic substances insoluble in water and having no soluble salts, the *humin* fraction. The proportions of these four fractions vary appreciably according to the origin of the humic matter, but the humic acid fraction always predominates in soils and peats. This fraction has therefore been more completely studied than the others. None of the fractions shows any traces of crystalline character.

The chemical investigation of the humic acid fraction has proceeded along two main lines. In studying its chemical reactions the classical methods of the organic chemists have been beset with such difficulties that argument by analogy has all too often been invoked. Thus the naturally occuring humic acid has been compared and identified at different times with a whole series of artificial products which can easily be prepared in the laboratory, and which have, so far as outward appearance goes, the same general properties. We now know that none of these is identical with the naturally occurring humic acid, with the possible exception of that from lignin (see below). The second line of attack has been more direct, and so far as soil humic acid is concerned, more successful. Something may be learned from the elementary composition of humic acids, particularly when the figures are placed alongside those of the plant materials which are the possible parents of humic matter. Such figures are presented in Table VI. It is clearly apparent that the nitrogen content of humic acid from a mineral soil is much too large to be disregarded. Now it has been shown that the nitrogen is present in a protein-like combination. Therefore, since pure protein contains about one-sixth of its weight of nitrogen the soil humic acid must consist of some 32 per cent. of protein-like material and 68 per cent. of a different complex containing no nitrogen. The composition of this remaining 68 per cent. can easily be calculated using an average figure for plant protein. The result is given underneath the figures for the whole humic acid fraction.

TABLE VI

| Material. | % Carbon. | % Hydrogen. | % Nitrogen. | % Oxygen (by difference). |
|---|---|---|---|---|
| Peat<br>Humic acid . | 58·2 | 4·3 | 1·0 | 36·5 |
| Soil<br>Humic acid . | 56 | 5·1 | 5·4 | 33·5 |
| „ „ without protein . | 57 | 4·1 | 0·0 | 38·7 |
| Plant protein . | 52 | 7·0 | 16·0 | 25·0 |
| Cellulose . . | 44·4 | 6·2 | 0·0 | 49·4 |
| Lignin . . . | 69 | 6·0 | 0·0 | 25·0 |

Comparing it with the values for cellulose and for lignin, it is seen to be intermediate so far as carbon and oxygen are concerned but lower than either in hydrogen.

It might be expected, therefore, from these considerations, that the humic acid fraction could be regarded as a physical mixture of protein with a non-nitrogenous constituent. This view is, however, untenable. Although many methods of separation, both physical and chemical, have been tried, none has split the nitrogenous from the non-nitrogenous. Even in cases where a valid fractionation of the humic acid has been attained, the nitrogen has been divided proportionately between the fractions. We must therefore regard the nitrogenous part as being firmly and intimately combined with the non-nitrogenous part.

The investigations have been carried a stage farther by experiments on the decomposition of known plant constituents when added to soil. The idea has been to trace a possible connection between the disappearance of some plant constituent and the appearance of the humic acid fraction. These experiments have their own special pitfalls, but in spite of the analytical difficulties one conclusion of importance has emerged. It is certain that plant lignin is a parent of soil humic matter, and probable that the other plant constituents (except, of course, the protein) if they contribute to it at all, do so only in a minor degree.

The close relationship between soil humic matter and lignin is also apparent in certain of their chemical reactions. A description of these would be out of place here, but it may be recalled that lignin itself is an aromatic compound with a benzene nucleus and characteristic side chains. Its exact structure is still debated.

In attempting to obtain a perspective view of the part played by humic matter in the soil it should not be forgotten that its production and also its decomposition are due to the activity of soil micro-organisms. A considerable part of it must at some time during the breakdown of the original plant material, have formed the protoplasm of these micro-organisms. Most of the nitrogen in humic matter has probably passed through this intermediate stage.

The function of humic matter as a reservoir of plant nutrients depends on several different properties. Thus it can retain calcium, magnesium, potassium and sodium by virtue of its salt-forming capacity, and these cations can be liberated just as they are from clay by base exchange. Weight for weight, soil humic matter has from three to seven times the base exchange capacity of the clay fraction. It also acts as a source of nitrogen, sulphur and phosphorus which are all constituents of the organic complex and are liberated as simple compounds when this is decomposed by micro-organisms.

**The Colloidal Properties of Humic Matter.**—We may consider, firstly, the conditions under which the four fractions of soil humic matter may enter and leave the colloidal realm.

The fulvic acid fraction is, as we have already noted, soluble in water, giving a yellow or brown solution which passes the usual ultra-filters. The colour darkens when the soluble sodium, potassium or ammonium salts are formed. The formation of the calcium or magnesium salts causes precipitation and, so far as we can judge from the scanty data, these salts do not readily peptize to form stable sols.

The hymatomelanic acid fraction is insoluble in water but soluble in alcohol. Stable sols in water can be prepared in two ways ; either by pouring the alcoholic solution into a large volume of water or by precipitating the acid in water and then washing out the added free acid and the salt produced, by distilled water. When the concentration of soluble acid has been sufficiently reduced, the hymatomelanic acid peptizes to give a stable brown sol, similar in appearance to that prepared by the first method. The sodium and potassium salts of hymatomelanic acid are soluble in water but insoluble in alcohol. The calcium and magnesium salts are insoluble both in water and in alcohol. Hymatomelanic acid, with an equivalent weight of about 200 has a very high base exchange capacity.

The humic acid fraction is insoluble in water and in alcohol. It very readily passes into the sol by peptization when the precipitate obtained by adding an acid to sodium humate solution is washed with distilled water. To a slight extent it also peptizes in alcohol, so that the hymatomelanic acid fraction generally contains some colloidal humic acid which can be removed by an ultra-filter. The sodium, potassium and ammonium salts are soluble in water, the calcium and magnesium salts being insoluble and not easily dispersed when once precipitated. Its equivalent weight is about 300–350, and its base exchange capacity, though high, is correspondingly lower than that of hymatomelanic acid.

The humin fraction resembles colloidal clay. It never goes into true solution, and, so far as it is known, it only gives stable sols when sodium, potassium or ammonium are the exchangeable cations present. For this reason it has so far proved impossible to separate it from clay, and it can only be studied in a reasonably pure state when prepared from sandy soils or from peats. Very little is known about this fraction, but it is probable that its base exchange capacity lies between that of the humic acid fraction and that of the clays.

Most of the colloid-chemical researches on the properties of humic matter have been carried out on the crude mixture of the hymatomelanic and humic acid fractions which is obtained by acidifying an alkaline solution from peat. No quantitative studies have been made to determine how far the properties of soil humic matter, with its much greater nitrogen content agree with those of peat humic matter.

The coagulation of sols of humic acid and of calcium humate closely resembles that of clay sols in its general features. The sensitivity of humic acid towards coagulating agents is, however, considerably less than that of the clays, and calcium humate is rather less sensitive than humic acid.

The adsorption of humic acid and of the soluble humates at surfaces is strong. This adhesion, together with their small sensitivity towards coagulating agents, causes humic acid and the humates to act as protective colloids. In this respect they are to be regarded as comparable with gelatin, starch, etc. It has been shown that 1 gram of colloidal clay may be completely protected by 10–20 milligrams colloidal humic acid up to the point at which humic acid itself is coagulated. Now humic acid is coagulated by amounts of electrolyte which are seldom more than ten times those required for clay. Thus the effectiveness of humic acid and the humates as protective colloids is displayed over a much narrower range than that of gelatin. Nevertheless, it is of great importance in soils and the subject is worthy of much closer study than it has yet received.

When water is removed from flocculated humic acid or from calcium humate a point is soon reached at which a black, non-elastic gel is formed. This shrinks enormously on drying and eventually becomes a brittle solid. The process resembles the drying of silicic acid gel, and the brittle black humic acid, like dried silicic acid, does not pass back again into the sol form when water is added. While the gel is still soft and moist it readily expands to its original volume on addition of water, and eventually peptizes to give a sol. The contraction and expansion of peat under natural conditions is a very well-known effect. In dry weather great cracks and fissures appear, accompanied by a drop in the surface level As the peat bed once again becomes saturated with water the original condition is restored. It is seldom that peat beds become so dried out that the irreversible stage is reached, but there is a strong probability that the humus in the surface layer of certain cultivated soils in dry regions will actually attain it.

The loss of water vapour from humic acid gels and from peats has been studied. The curves are of the same form as those for clay, and it is a remarkable fact that humic acid and calcium humate show practically identical behaviour. It may be concluded, therefore, that the liming of peaty soils will make little difference to their affinity for water.

Having discussed the composition and reactions of clays and of humus, we have now reached a convenient point for a brief summary of the ways in which the common plant nutrients are retained by the soil and finally liberated. Potassium, sodium, calcium and magnesium are held as exchangeable bases and are liberated by cation exchange. In this process the humic matter is about five times as active as the clay. It will be recalled that calcium is the predominant exchangeable cation in fertile soils. When potassium, sodium or magnesium salts are applied to the soil an equivalent amount of calcium is liberated and appears in the drainage water along with the anions of the salts employed. When the potassium, sodium or magnesium ions are finally absorbed by plants their places are taken either by hydrogen ions or calcium ions ; the latter alternative is only possible where the soil has reserves of calcium carbonate.

Phosphorus is held chiefly in some inorganic combination associated with the clay, but it is also a regular constituent of humus. Minute traces only are found in the drainage water. The mechanism of its liberation from clay for intake by plants is not known. It appears as the phosphate ion when the soil organic matter undergoes complete oxidation.

Nitrogen can only be retained for long periods when it is in organic combination as part of the humic matter. From ammonium salts the ammonium cation is taken up by base exchange in which the clay and the humus are both concerned, but nitrification rapidly transforms it into the nitrate anion which passes into the drainage water unless taken up by growing plants. The decomposition of soil organic matter slowly liberates ammonium salts which again are rapidly transformed into nitrates.

In considering the action of mixed or compound fertilizers the fate of each ion present should be dealt with separately, remembering that all cations will undergo base exchange if this is possible, and that all anions will pass into the drainage water, with the important exception of the phosphate ion. The exchangeable base status of the soil itself should also be taken into account.

### SUPPLEMENTARY READING

The three modern textbooks on soils, N. M. Comber's *An Introduction to the Scientific Study of the Soil* (2nd ed., London, 1932), E. J. Russell's *Soil Conditions and Plant Growth* (5th ed., London, 1933), and G. W. Robinson's *Soils* (London, 1932), all emphasize the importance of the colloidal nature of humus for the soil. They do not attempt to give all the chemical evidence on the constitution of humic matter and its relationship to lignin. This is to be found in H. Strache and R. Lant's *Kohlenchemie* (Leipzig, 1924) and in many original papers published in *Die Brennstoffchemie.* On the other hand, modern work on the microbiology of humus by Waksman and his collaborators may be followed in the pages of *Soil Science* from 1927 onwards.

## CHAPTER IX

# COLLOIDS IN SOIL FORMATION PROCESSES

No attempt has been made in these pages to disguise the fact that in many cases the study of soil colloids in the laboratory is carried out under entirely different conditions from those which obtain in the field. This is especially true in dealing with the processes of soil formation and development. It will be recalled that in dealing with the subject of the formation of colloids (Chapter II), it was only possible to trace general tendencies, not exact quantitative laws. Now soil colloids are formed under conditions so difficult to define, that we cannot even separate the most potent of the factors which have played their part. Yet it is easy to see that the mineral colloids of soils may have been formed in three different environments.

The production of a colloidal clay in the soil itself involves a series of reactions in the most complex and variable of these three environments. Disregarding, for the moment, the important influence of climate and that of vegetation, we have to consider how the well-defined minerals which we recognize in the rocks are transformed in situ into the much less clearly defined group of the clays. The first stage in this process is known, at any rate as regards the felspar group of minerals which constitute 60–70 per cent. of the primary rocks of the earth's surface. Under the influence of rainwater these minerals lose calcium, sodium and potassium at an appreciable rate. The reaction appears to be simple. Hydrogen ions from the water displace sodium, potassium and calcium ions from the lattice. The presence of carbonic acid in the water, by increasing the hydrogen ion concentration, hastens the reaction. For the same reason, hot water is more effective than cold. Taking orthoclase and albite as typical examples, we have the following equations :

$$K_2[Al_2Si_6O_{16}] + 2H^+OH^- \rightleftarrows H_2[Al_2Si_6O_{16}] + 2K^+OH^-$$
$$Ca_2[Al_4Si_4O_{16}] + 2H^+OH^- \rightleftarrows H_4[Al_4Si_4O_{16}] + 2Ca^{++}(OH^-)_2$$

From this point onwards, however, we have no exact knowledge of the processes which eventually lead to the production of the clay minerals. It is supposed that the hypothetical minerals represented on the right-hand side in the above equations readily decompose, giving free silicic acid and clay minerals such as kaolinite $H_4Al_2Si_2O_9$ ; but it is by no means certain how the silicic acid is subsequently removed. The change in crystal structure in passing from the felspar to kaolinite is considerable, but so far as we know, it occurs in situ and not by crystallization from solution. The production of a kaolinite clay is not the only type of change caused by the weathering of primary rocks. Under tropical conditions and from the more basic rocks, which consist chiefly of albite with iron-magnesium silicates, the residual product is a mixture of aluminium and iron hydroxides. This is known as *laterite.* Under less extreme conditions, in which the loss of silica is not so great, clays result which strongly resemble the true laterites in appearance but which contain combined silica. They are generally more highly colloidal than the true laterites. Their mineralogy still awaits detailed study.

From the rocks certain constituents are, as we have seen, brought into solution, and they eventually appear in the streams and rivers. This is the second environment we have to consider. Here the conditions approach more nearly those of the laboratory. The presence of bases ($Ca(OH)_2$, NaOH, KOH) and of silicic acid follows from what has just been said. Aluminium hydroxide is also an important constituent and it is brought into solution when the felspars encounter somewhat more acid solutions. Such solutions are provided by the decomposition of vegetation. Ferric hydroxide is also present. All the elements are therefore available from which the clay minerals may be synthesized. The dilutions of all constituents are high, thus crystallization will be slow and it may be hindered by such temporary associations as can be formed by the mutual coagulation of positively charged aluminium hydroxide with negatively charged silicic acid sols. It is believed that these conditions are favourable to the formation of base-exchange clays such as beidellite.

Where the river finally empties into the sea a third environment is encountered. Here there is a high concentration of salts and the colloidal material brought down by the rivers is coagulated. It is deposited as mud, along with the unchanged mineral grains derived by purely mechanical action from the original rocks. In such deposits the rebuilding of aluminosilicate structures certainly proceeds, but at a slow rate because of the much smaller solubility of their chief constituents in sea water compared with river water. The sediment finally produced has normally a higher ratio of silica to bases than the rocks from which it is derived. In this way clays of secondary origin are formed, whose mineralogical composition seems, so far as our limited knowledge goes, to be dominated by beidellite or by montmorillonite.

The production of clays by the purely mechanical disintegration of rocks is also very important and it reaches its greatest intensity in glacial regions. Here the chemical transformations are at a minimum in consequence of the low temperature, and the boulder clays primarily formed consist almost entirely of unchanged rock fragments. As might be expected, the particle size is greater than that found in the sedimentary clays and the clay minerals themselves are absent. Thus the glacial clays derived from primary rocks consist chiefly of felspar fragments varying in size from about 0·2 $\mu$ upwards. They possess notable reserves of bases, the greater part of which are only very slowly made available.

So much for the physical and mineralogical conditions which operate over geological periods of time. In order to form a clear picture of the details of soil development under the influence of climate and vegetation we must digress for a moment to introduce a fresh conception of the surface of clay particles. So far, in dealing with surfaces, we have ascribed to each a single type of dissociation, leading to the production of a negatively or positively charged particle as the case might be. But in the silicates we have structures which contain both silicon and aluminium atoms at the surface. Now silicon dioxide has a negatively charged surface whilst aluminium oxide gives a positively charged one (except in alkaline solution where it also is negative). The properties of mixed surfaces, such as those of the clays, will therefore depend (*a*) on the relative properties of the constituent atoms and (*b*) on the strengths of their respective capacities for ionization, and these factors will operate in the same general sense whether the surfaces under consideration are crystalline or not. Surfaces with this kind of dual function are described as *amphoteric.* Since the two kinds of ionization are mutually antagonistic (the one tending to drive positive ions into solution whilst the other liberates negative ions), there will be some point in the range from extreme acidity to extreme alkalinity at which the two types of dissociation just balance. At this point the surface as a whole will be uncharged; it is therefore called the isoelectric point. The system, if colloidal, is here completely coagulated and its water-holding capacity is at a minimum. The only soils which occur naturally in an isoelectric condition are certain lateritic types in which the proportion of silica to alumina is small. The isoelectric point is here only slightly on the acid side of the neutral point. Where the proportion of silica is high the isoelectric point lies well over the acid side, and so under natural conditions the colloidal clay carries a negative charge; except in so far as this may be reduced to zero by the presence of coagulating ions like $Ca^{++}$. Soil humic matter generally has a high negative charge and it shows no amphoteric properties.

**Soil Development under Arid Conditions.**—The entire story of soil development processes is best considered by describing the changes encountered in passing from the driest to the most humid climate.

Under desert conditions where rainfall is negligible in amount, it is evident that chemical decomposition can only play a very minor part. Physical weathering is here largely due to sudden temperature changes and the agent of transportation is wind. The soils will chiefly be sands containing little or no colloidal matter unless such material had previously been laid down earlier in the same region when the climate was less dry.

Under less extreme conditions, in which the rainfall is sufficient to allow of plant growth, at any rate during part of the year, whilst evaporation is very high, quite different soils are produced. The water which saturates the soil during the rainy season has only limited opportunities for draining away because of the high rate of evaporation following. During the evaporation the water is continually replenished from below and the substances held by it in solution are deposited at the surface of the soil. Thus the clay material present is brought into contact with stronger and stronger solutions, chiefly of sodium salts. The calcium present in the soil water is transformed, on evaporation, from the soluble calcium bicarbonate to the very slightly soluble carbonate, another portion being deposited as gypsum (calcium sulphate). In the upper layers, therefore, the concentration of calcium ions will be low and practically constant, whilst that of the sodium will tend to increase. The colloidal clay itself will reflect this change; it will take up sodium as the exchangeable cation, releasing some of its calcium. A mixed sodium-calcium clay is thus produced. Such a clay is of a more sticky, impervious nature than a calcium clay and is characterized by the formation of a hard crust in dry weather. Agriculturally, therefore, these soils present very difficult problems in cultivation. In extreme cases the accumulation of salts in these *saline*, or *white alkali* soils makes plant growth impossible.

The washing out of the soluble sodium salts leads to further undesirable changes. The sodium clay then reacts with calcium carbonate to give sodium carbonate and calcium clay so that a strongly alkaline reaction is attained, sufficient to inhibit plant growth. The sodium carbonate dissolves humic matter which is brought to the surface and causes these soils to be described as "*black alkali.*

Both types of alkali soils are developed chiefly in valleys and depressions where there is a comparatively high water table, since in such situations the salts are accumulated from a considerable drainage area. They are described by various names. The saline soils are known as solontschak in Russia, white alkali in the United States, and usar in India, whilst the alkali soils are solonetz in Russia, black alkali in the United States, and szik in Hungary.

The reclamation of such soils is a very difficult task. Irrigation only solves one part of the problem. Unless very efficient drainage can also be arranged it may even accentuate the trouble, by causing a permanent rise in the water table. Further, in regions where these soils occur, the water available for irrigation generally contains a preponderance of sodium salts, so that although it may remove the large excess of sodium salts originally present, it does nothing to bring the soil to a better physical condition. The clay remains a sodium clay. For this reason chemical treatments are usually combined with irrigation. The application of gypsum has been successfully tried in the United States. The gypsum provides a soluble reserve of calcium which will, after the bulk of the sodium salts has been washed away, convert the sodium clay into the more tractable calcium clay, this being, under field conditions, entirely flocculated.

(Less difficult reclamation problems are presented by salt marches and the Dutch polders in humid climates. The soil, generally a rich alluvium, has, when first drained, sodium as its chief exchangeable cation. If the soil contains good reserves of calcium carbonate, exposure to normal rainfall is sufficient in very few years, to convert it to a calcium-saturated soil. The Dutch find that a crop of potatoes can be taken five years after drainage, during which time a good grazing pasture is established.)

**Soil Development under Semi-Arid Conditions.**—Passing from the desert and the semi-desert soils to those more favourable to plant life we encounter first the chestnut-coloured earths and then the very important group of the black earths, known as the *tschernosem* group. Here the rainfall is sufficient to remove all soluble salts, but at the same time the dry season is sufficiently intense to cause the deposition of calcium carbonate and calcium sulphate, which tend to accumulate in definite horizons. The depth of this accumulation varies with the climate and with the character of the soil. The dark character of these soils is due to humic matter, but the amount present is less than one would expect from the colour. It is possible that in the dry season the humic matter becomes so extensively dehydrated that it no longer takes up water to form a gel when remoistened. The great wheat-growing areas of the world are centred in and around the black earths; in Russia, in Argentina, in Canada and in the United States.

**Soil Development under Humid Conditions.**—The formation of lateritic soils in the tropics has already been discussed in connection with the weathering of rocks. It should be noted that a quick and complete decomposition of plant remains is essential to the production of laterites.

The accumulation of humic matter in the soil causes entirely different processes of soil development to arise. In passing from the black earth region to colder and moister climates the group of soils known as the brown earths is first encountered. Here the rainfall is sufficient to cause a continuous leaching out of calcium, in the form of calcium bicarbonate. The surface layers lose any reserve of calcium carbonate they may originally have possessed. The accumulation of humic matter, which is possible with the cooler climate, combined with the continuous, though not excessive leaching by rainwater, produce a soil possessing a slightly acid reaction in the surface layer. The development of a definite soil profile is, however, completely arrested by the operations attendant on systems of arable farming, which cause mixing of the layers. Most of the soils in Great Britain, especially those of a medium or heavy type belong to this group. They show some lime deficiency in the surface layers, but have not lost all their reserves of exchangeable calcium. Under deciduous forest a soil *profile* (that is, a vertical section) showing definite layers or horizons is formed. The top layer with much humus is dark brown, then follows a brown layer and finally the original subsoil is reached. In some American brown earths colloidal clay has been carried down into the second layer, but its composition remains unaltered.

**Podsol Formation.**—With a further fall in mean temperature and a further increase in rainfall a very marked accumulation of humic matter becomes possible. It has a profound effect on the soil profile and leads to the formation of the *podsol* type. The acid nature of the humic matter which is continually being produced, combined with the high precipitation, cause the removal of all reserves of calcium from the surface layer, so that the clay and the humic matter are practically completely saturated with hydrogen ions. Moreover, in the undisturbed condition humic matter is continually being added at the surface, giving a layer almost free from mineral matter. As rainwater percolates through this layer it takes up humic acids by peptization and organic water-soluble acids of varying degrees of complexity by solution. The layer of mineral matter immediately below then comes into contact with this acid liquid. Now the clay in this layer is already a hydrogen clay and we have several lines of evidence which point to the fact that hydrogen clays are inherently unstable. (Thus on treatment with neutral salts they liberate, not only acid, but aluminium as well. Further, notable amounts of aluminium and iron are carried to the negative electrode when an electric current is passed through a hydrogen clay suspension.) The combined effect of the nature of the percolating water and the instability of the hydrogen clay is that a transportation downwards of iron and aluminium hydroxides with some silica occurs. The residual mineral matter then takes on a greyish bleached appearance. It contains less of the clay fraction than it possessed originally, and what clay remains contains a higher proportion of silica. The transported material is deposited in one or two layers immediately following. In the iron podsol there is only one layer, brown in colour, in which deposition occurs. In the humus podsol there are two layers; a black layer of humus, immediately below the bleached mineral layer, and following that a brown layer containing the transported mineral matter. The brown layers contain a higher proportion of clay than the original soil and this clay is considerably richer in iron and aluminium hydroxides. The exact mechanism of podsol formation has not been completely elucidated, but the following three effects can readily be demonstrated in the laboratory; (*a*) that humic acid sols exert a protective action on clay particles, (*b*) that solutions of organic hydroxy-acids bring iron and aluminium into solution and that such acids are produced by the decomposition of peaty material under acid conditions, (*c*) that hydrogen clays are unstable (see above). In Table VII the extent of the change caused by podsol formation is illustrated by full details of a typical example.

## TABLE VII

Analytical Data for a Podsol (Owen and Davies)

| Horizon. | % Carbon. | % Clay Fraction. | Ratio $\frac{SiO_2}{Al_2O_3 + Fe_2O_3}$ for Clay Fraction. |
|---|---|---|---|
| Peaty $A_0$ . . . | (Leaf Mould.) | | — |
| Bleached $A_2$ . . | 1·63 | 1·3 | 4·56 |
| Black $B_1$ . . . | 7·14 | 8·8 | 1·48 |
| Brown $B_3$ . . . | 0·40 | 2·2 | 1·30 |
| Unchanged Subsoil C | 0·04 | 3·3 | 2·31 |

This brief review of soil formation processes only indicates in the very broadcast outline the range of soil types. It is, however, sufficient to show that the relationship between climate and prevailing vegetation must be to a large extent governed by the influence which the climate has already exerted on and through the agency of the colloidal material present in the soil. The soil type represents a more or less temporary equilibrium in the interaction between soil and climate. Agriculture, by its systems of cropping, by cultivation and manuring disturbs this natural equilibrium. When intelligently practised, as it generally is under conditions of greatest difficulty, a marked improvement of the soil may result. But in circumstances where the original soil type is favourable, an unintelligent and grasping system of agriculture can cause such serious deterioration that after a few years the land is left derelict. These facts are familiar to every agriculturist and they clearly imply that in the development of virgin tracts the scientist should precede the farmer and should determine in advance the system of agriculture to be followed.

### SUPPLEMENTARY READING

G. W. Robinsons *Soils* (London, 1932) contains the only complete yet concise account of soil types and their development published in English. In German there is Glinka's *Typen der Bodenbildung* (Berlin, 1914) and also G. Wiegner's fine monograph *Boden und Bodenbildung in kolloidchemischer Betrachtung* (Leipzig, 1919). E. Ramann's *The Evolution and Classification of Soils* (Cambridge, 1928) is a translation of a monograph published in German in 1917.

## CHAPTER X

## COLLOIDS AND SOIL TEXTURE

**Soil Colloids and Cultivation.**—The art of cultivation as practised and improved by countless generations of farmers has as its chief object the attainment of the physical soil conditions best adapted to the growth of crops. These conditions include the maintenance of an adequate supply to the roots both of air and of water, and it is the difficulty of fulfilling the two at once which has made the practical operations so diverse and so full of skill. On whatever kind of soil he works, the agriculturist has an ideal before him; that of a loamy soil, deep and friable, having a crumb structure strong enough to stand against the wind and the sudden downpour, yet yielding readily to his implements in the making of the seed-bed. He approaches this ideal by an unconscious manipulation of the colloidal material which lies under his hand.

So important to the agriculturist are the physical characteristics of the soil, that his own classification of soil types is based on the resistance offered to the passage of his implements. The terms light, medium or loamy and heavy are used in this sense. There is naturally no attempt to classify by any absolute standard. The words are relative only, so that loamy soil of medium texture might in a region of light soils be described as heavy and in a region of heavy soils as light. Further, there are a number of soils having special characteristics for which other terms are more descriptive. The two classes of soils rich in humus, namely peat and fen, are distinctive; so also are the highly calcareous soils. In the humus soils the colloidal properties of the humic matter completely dominate the physical character. For this to occur it is not necessary that the humic matter should be the major constituent. Soils with 20–50 per cent. of humic matter are included in the group along with those having 50–100 per cent. This strongly dominant character of the humic matter makes a small percentage of it often sufficient to transform what might be an infertile sand into a good light soil. Here both its high base exchange capacity and its beneficial physical properties contribute to the improvement.

In the case of mineral soils having only a low content of humic matter, the mechanical analysis adds considerably to our knowledge of soil texture. The clay fraction is of greatest importance in determining the physical character, then follows the silt fraction and lastly come the fine and coarse sand. Some typical examples are given in Table VIII.

It should be realized, however, that such figures can only properly be compared with one another when soils belonging to the same general type are under consideration. It would be wrong to conclude, for instance, that a lateritic soil giving the same percentages as the heavy English clay soil of Table VIII would show the same resistance to the passage of implements. The chemical and mineralogical nature of the clay fraction cannot be entirely disregarded. Again, the contribution of the humic matter to the colloidal properties of the soil is entirely

TABLE VIII

MECHANICAL ANALYSIS FIGURES FOR SOME YORKSHIRE SOILS

| Soil Type. | Cropping. | Coarse Sand. | Fine Sand. | Silt. | Clay. |
|---|---|---|---|---|---|
| Light sand . . | Potatoes and barley | 56·09 | 29·81 | 2·88 | 6·12 |
| Alluvium (Warp) | Potatoes and sugar beet | 0·50 | 45·25 | 29·35 | 9·65 |
| Alluvium (Warp) | Wheat and beans | 1·33 | 31·26 | 21·50 | 25·70 |
| Medium loam . | General arable | 8·97 | 45·91 | 15·97 | 18·83 |
| Heavy clay . . | Grassland | 1·49 | 5·32 | 12·45 | 64·00 |

ignored by the mechanical analysis figures, and this is, as we have seen, a most serious omission.

For these reasons, therefore, soil physicists have devoted considerable attention to the exploration of other methods of expressing soil texture which are capable of approaching more nearly to the field conditions. In these methods the whole soil, including the humic matter, is used.

**The Dynamometer.**—This is the measuring instrument par excellence for field studies of soil resistance. In its simplest form it consists of a spring balance placed between the source of power and the implement, with a dial which registers the tension. At Rothamsted a much more accurate type has been developed which makes a continuous permanent record as the implement travels. With this instrument on the heavy Rothamsted soil (clay with flints) the following important facts have been established. (1) On areas receiving the same treatment the resistances at different points always bear the same relationship to one another. (2) Within the limits normally observed for cultivation operations there is practically no change in resistance with the moisture content of the soil. These two observations make it possible to map arable areas so as to show the *isodynes* (lines of equal soil resistance) as permanent features. (3) There is evidence that the accumulation of humic matter caused by heavy dressings of dung has produced an appreciable reduction in soil resistance. This amounts to no more than 10 per cent. with dung applied at the rate of 14 tons per acre. This heavy application continued over a period of eighty years had raised the content of humic matter from about 2 per cent. to 6 per cent. (4) Very heavy dressings of chalk also lower the resistance. A small excess of lime or chalk over and above that required to neutralize acidity shows no measurable reduction. These observations have not yet been extended over a sufficient range of soil types to enable one to lay them down as general rules.

**" Single Value " Soil Constants.**—It is difficult to see how any laboratory measurement can replace a direct determination of soil resistance in the field and none has yet been devised which comes within measurable distance of doing so. We have already noted some of the complex factors concerned in soil texture : the proportions of particles of different sizes, the chemical and mineralogical nature of the clay fraction, the amount of humic matter, the nature of the exchangeable cations, the presence or absence of coagulating agents, the previous history of the soil. Add to these the fact that the passage of a rigid body through a soil involves physical forces which are not understood and which can only be separated from one another in a very arbitrary way, and it will readily be seen that the chances of a simple laboratory experiment expressing quantitatively the field behaviour are so remote as to be negligible. For this reason the various physical constants which are used for the characterization of soils will be considered here purely from the colloid-chemical standpoint.

**Moisture Relationships.**—It will be recalled that although the vapour pressure-moisture content relationships of clay and of humic matter show a decided similarity, there is one important difference between them, namely, that the drying of humic matter beyond a certain point leads to irreversible changes, so that subsequent addition of water no longer brings one back to the original gel. This happens for comparatively high values of the vapour pressure. In the laboratory the humic acid fraction attains the irreversible state by drying under ordinary atmospheric conditions. Whether this is also true of the total soil humic matter in association with the clay is not known, but it is highly probable in hot dry climates.

Since the adsorption of water vapour is so well marked in both clay and humic matter many attempts have been made to assess the total colloid content by a determination of adsorbed water. This, unfortunately, cannot be done with any accuracy. Neither in clay nor in humic matter is it possible to distinguish between adsorbed water and chemically combined water ; the curves for low vapour pressures show no breaks. Equally serious is the fact that no distinction is possible between adsorbed water and liquid water contained in the minute interstices between small particles. This is due to the fact that concave liquid surfaces have a lower vapour pressure than a plane surface. For each value of the vapour pressure there exists therefore a certain critical radius, and every capillary smaller than this may contain liquid water. Thus the taking up of water vapour from a saturated atmosphere consists of two processes—the adsorption proper and the filling up with liquid of the smallest capillaries. It is this slowly acting second factor which makes the attainment of a true equilibrium impossible in a saturated atmosphere.

The moisture content as determined on air-dry soil represents very nearly the water lost in passing from a half-saturated atmosphere at room temperature up to a similar vapour pressure value at 110° C. Since at half-saturation equilibrium is reached fairly quickly, there is probably little capillary water involved. The distinction between chemically combined and adsorbed water is so highly artificial as to be meaningless in the case of clay and humus particles, which probably contain minute internal capillaries holding both water and exchangeable cations. That does not, however, make the moisture content determination any less valuable ; for what we really require is a measure of the number and the potency of those molecules whose normal properties are modified by their presence at a surface. It is immaterial whether the surfaces are internal or external. Now the moisture content determination represents the number of water molecules which can escape from the surface under clearly defined conditions ; the only doubtful point being the behaviour of the surfaces of the humic matter at 110° C. Here, unfortunately, there is strong probability of permanent change and it would be better to use a temperature well below 100° C. An even more valuable figure is obtained by working at constant temperature and determining the moisture lost between, say, a half-saturated and a one-tenth-saturated atmosphere. Such experiments alone do not enable one to separate the contributions of the mineral and the humic matter, but removal of the latter by mild oxidizing agents followed by a redetermination under the same conditions allows one to compute approximately the separate values.

The loss on ignition is less clearly related to the colloidal properties than the moisture content. It is given by the total loss between 110° and red heat. The whole of the humic matter is oxidized, the adsorbed water is all driven off and the clay minerals lose water not only from the internal and the external surfaces but also from OH groups forming an essential part of the lattice. Thus the surface molecules are only a small fraction of those affected. Hence the loss on ignition is more valuable as a criterion of the amount of organic matter in peaty soils than as a measure of the colloidal character of mineral soils.

As we traverse the range from completely dry to completely wet soil we encounter a bewildering series of so-called constants, in which part of the capillary or " free " water is included along with that held by adsorption. These constants have been much discussed in soil literature. It is obvious that a large proportion of small particles implies a larger number of small capillaries, so that the amount of water held by the soil against a given force tending to suck it away will increase with the percentage of colloidal matter. Various devices have been used to suck away the water. Living plants have been employed and the moisture content at which wilting occurred has been taken as a characteristic soil constant (the *wilting coefficient*). Unfortunately, it depends on the type of plant and its environment as well as on the soil. The centrifuge running under standard conditions has also been used, giving a value known as the " *moisture equivalent.*" By taking another liquid such as xylene and subtracting the xylene equivalent from the moisture equivalent a value is obtained which corresponds to the moisture held in close association with the soil colloids, since the xylene only fills the larger pores (the "*Imbibitional Moisture*"). Instead of centrifugal force, atmospheric pressure has been used, giving a higher " moisture equivalent " than the centrifuge. Gravity affords a still smaller suction and the moisture content of a soil from which the excess water has drained is termed the "*maximum capillary water capacity*." Finally, when the force falls to zero and no water is removed we have the "*pore space*" determination. This last value lies very close to the "*sticky point*" which is the moisture content of a kneaded mass of soil plus water when it is brought into such a condition that it just ceases to stick to the fingers.

**Seasonal Variations in Physical Conditions.**—The important influence of climate on soil colloidal matter throughout the world has already been discussed, but to the practical agriculturist the seasonal variations in the character of his own soil are of more immediate interest. Several effects have already been noted; the shrinkage of clay on drying out and its subsequent break-up when remoistened, the reversible shrinkage of humus and its final assumption of an irreversible non-gelatinous condition if the drying process has proceeded beyond a certain point. It remains to consider the effect of frost and the subsequent thaw. The expansion of water on freezing loosens the coherent soil blocks or crumbs and, as is well known, these fall apart in the thaw. Apart from this fairly obvious mechanical action it is often stated that part of the beneficial action is due to a coagulating action of frost on the soil colloids. Such coagulations are readily observed when dilute suspensions of clay or of humic acid are frozen. They are ascribed to the increase in salt concentration in the residual liquid caused by the separation of pure ice. Since under normal conditions most soils are already in a coagulated state and the individual particles have no appreciable mobility, such a coagulating action could only be made manifest by an increased adhesion between them. One would expect, however, that in the thaw the original condition would be restored. There is a third effect to consider, namely, the dehydration of the colloids.

At temperatures below 0° C. water will freeze which has normally a lower vapour pressure than that of ordinary water. From the relationship between lowering of vapour pressure and freezing-point one can calculate, for instance, that at —18° C., water molecules having only one-third the vapour pressure of normal water will be capable of forming ice. The formation of ice crystals is thus equivalent to a dehydration of the soil colloids. The extent of this effect will depend on the temperature attained, but it will not necessarily correspond to the calculated value because in fine capillaries the attainment of a true equilibrium may be extraordinarily slow. Still, some measure of dehydration and therefore of shrinkage of the colloidal particles, is to be expected. But in freezing, the soil as a whole expands, due to the expansion of the capillary water. Thus the shrinkage of the colloidal material can only occur in very small units and any permanent changes observed might be due to a reluctance on the part of small colloidal aggregates to pass back to their original state of hydration.

**The Influence of Fertilizers on Soil Texture.**—Instances have already been given of the chemical changes caused by the application of fertilizers. The accompanying physical changes are readily understood. Long-continued application of sodium salts causes the replacement of exchangeable calcium by sodium and since both clay and humus tend to disperse when sodium is the outer cation the colloidal character of the soil alters in the direction of greater dispersion and greater hydration. The stickiness which develops on nitrate of soda plots is thus explained.

A marked improvement in texture is also held by practical agriculturists to follow the application of lime to acid soils. As regards drawbar pull, we have already noted that the Rothamsted experiment failed to show measurable reduction unless the amount of lime was very greatly in excess of that needed to displace the exchangeable hydrogen. Nevertheless, the smaller applications normally used may have some effect on the tilth, as, for instance, by increasing the stability of the soil crumbs. It should be remembered that whereas the calcium and hydrogen clays are very similar in their capacity for dispersion and coagulation, humic acid is much more readily dispersed than calcium humate.

**Crumb Formation.**—The attainment of a soil condition suitable for the healthy growth of arable crops is largely a matter of aggregates of particles rather than of single particles. These aggregates or crumbs are much more stable in some soils than in others. In certain types the tendency towards their formation causes the undisturbed soil to have a characteristic nodular appearance, as, for instance, in the black earths. A stable crumb structure is a very valuable physical property. It is one of the most important factors in preventing soil erosion, as American workers have shown. The relationship between the size and the stability of soil crumbs and the properties of the colloidal material contained in them is, unfortunately, still obscure, but the subject is being pursued and already some interesting suggestions have been put forward.

This chapter may very aptly be closed by a brief description of one of the most elegant applications of the theory of colloids to the problem of soil resistance. In discussing the ionization of colloidal particles the effect of an applied electric field was shown to be that the colloidal particle moved to one pole, its atmosphere of ions to the opposite pole. If, however, the colloidal particle forms part of a rigid structure, then it is not free to move at all, and in order to preserve the relative motions of the different parts of the system the water molecules must move instead, and their direction of motion must be opposite to that of a free colloidal particle. Thus water will be transported along with the cations to the negative pole. (This phenomenon is well known in porous materials generally and is termed *electro-endosmosis.*) If the negative pole forms the friction surface of an agricultural implement such as the mouldboard of a plough, then the effect of passing an electric current will be that a film of water will continually be formed at this surface. The friction, previously largely of the solid-solid type, is now reduced to a lower value corresponding more nearly to the solid-liquid type. These expectations were realized in dynamometer trials at Rothamsted. The measured resistance showed a well-marked and sudden fall as soon as the current was applied in the proper direction. The magnitude of the reduction was not sufficient to make the method an economic one. An important conclusion may be drawn from the experiment. It is clear that this movement of water depends on the charge on the surface.

The Rothamsted soil in its natural state has a measurable charge in spite of the presence of calcium carbonate and exchangeable calcium. It is a coagulated system, but the ionic concentration in the soil water is evidently insufficient to reduce the surface charge to zero.

### Supplementary Reading

The only modern work dealing with the scientific aspects of soil cultivation is B. A. Keen's *The Physical Properties of the Soil* (London, 1931).

# PART III

# *COLLOIDS IN PLANT AND ANIMAL LIFE*

## CHAPTER XI

## SOME COLLOIDAL MATERIALS PRESENT IN LIVING ORGANISMS

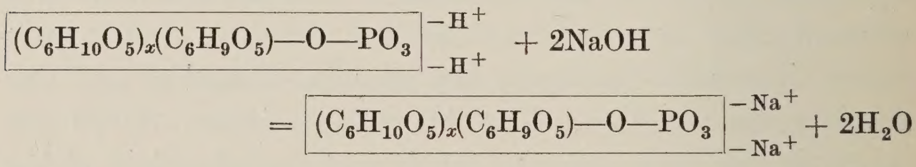
So great, so overwhelmingly predominant is the part played by surface molecules in the chemistry of life processes that the mind is stirred immediately to inquire as to the reasons for the completeness of this colloidal dominance. They follow at once from the most urgent needs of living organisms. In the simplest case these requirements are two in number. Firstly, a living cell must possess a high degree of permeability in order that the nutrients required may enter from outside and that waste products may be quickly eliminated. Secondly, it must have at least sufficient rigidity to maintain its own individuality. Each living cell must fulfil these fundamental conditions no matter how specialized its function. Now from the mechanical standpoint these two requirements are diametrically opposed to each other and it is only when we reach colloidal systems that a range of compromises sufficiently wide for the diverse needs of living matter is encountered. We have already found such systems in the gels, where the solid material, itself heavily hydrated, forms a continuous structure within which the water molecules are enmeshed. The great variation in rigidity and the smaller variation in permeability amongst the gels are caused by the operation of three main factors : (*a*) the hydration of the solid framework itself, (*b*) the amount of water enmeshed in it, (*c*) the structure and arrangement in space of the colloidal particles composing the framework.

Now in the isolation of colloids from living matter it is usually necessary to break down the original structure altogether and to change quite markedly the original hydration. Thus the study of purified colloidal systems in the laboratory does not necessarily lead to valid conclusions regarding the part played by these colloids in vital processes. It is merely the first step towards a complete understanding. A great deal of information of this kind is now available for the chief biological colloids. We shall consider it in the present chapter, which will be followed by a brief outline of the very remarkable progress made during the past few years in finding the structure of certain biological colloids under natural conditions.

## Colloidal Carbohydrates.

*Starch.* The occurrence of starch grains in green plants is universal and they constitute by far the greatest portion of the carbohydrate reserves which plants accumulate. In total amount, cellulose is probably a more abundant carbohydrate, but its function is chiefly structural. Starch grains themselves are too large to be described as colloidal particles. They range in size from 1 $\mu$ to 100 $\mu$ and may be either simple or compound in structure. Their shapes are to a large extent characteristic of the plants from which they are derived. They have the appearance, under the microscope, of having been built up by the deposition of concentric layers of material around a central nucleus. In the compound grains several nuclei have been concerned. Starch grains from different plants show a very close similarity in chemical composition; there being 80–85 per cent. of dry starch, 14–20 per cent. of water, 0·2–0·5 per cent. of mineral matter, and traces of fats.

The remarkable colloidal properties of starch only appear when the grains lose their identity by swelling, which occurs under the action of boiling water. Cold water has no action on them, a fact which led the earlier workers to the conclusion that the outer layers consisted of a resistant material resembling cellulose. Later work has shown that although two substances can be separated from starch grains, the differences between them do not warrant this assumption. Modern workers have split starch into two fractions, the amylose fraction and the amylopectin fraction. The latter constitutes 30–70 per cent. of the total starch. It is not certain that either is to be regarded as a pure chemical individual, but the differences between them are well marked. The amylose fraction shows no tendency towards gelatinization, carries no appreciable electric charge, can be completely freed from mineral constituents and gives a clear blue colour with iodine. The amylopectin fraction gelatinizes, carries a negative charge, is always associated with phosphorus and gives a violet colour with iodine. It has been shown that these marked differences are largely due to the presence of phosphorus which is combined as a starch-phosphoric acid. When the linkage between the two is broken, as it can be by long-continued boiling with water, the phosphoric acid can be removed by dialysis and the amylopectin loses its power of gelatinization and its electric charge. In fact, it only differs then from the amylose fraction by the colour it gives with iodine. On treatment with phosphoric acid recombination takes place and the original properties of the fraction are recovered. The amylopectin fraction of starch is thus to be regarded as a colloidal acid, and this conception helps to explain the action of dilute alkalis in promoting the swelling of starch. If the outer hydrogen ions of the electrical double layer are replaced by more strongly hydrated ions such as sodium, then an increased hydration is to be expected. The differences are similar in kind to those between a hydrogen and a sodium clay and the reaction could be represented like the cation exchange reactions which we have already encountered.



$$\boxed{(C_6H_{10}O_5)_x(C_6H_9O_5)\text{—O—}PO_3}\begin{matrix}-H^+\\ -H^+\end{matrix} + 2NaOH$$

$$= \boxed{(C_6H_{10}O_5)_x(C_6H_9O_5)\text{—O—}PO_3}\begin{matrix}-Na^+\\ -Na^+\end{matrix} + 2H_2O$$

The colours developed when starch fractions and their degradation products are treated with iodine have been much studied. No definite compounds have been isolated and it is concluded that the iodine is held by adsorption and that the particular colour developed depends on the degree of dispersion of the colloidal iodine which is precipitated. This, in turn, depends upon the effectiveness with which the carbohydrates can act as a protective agent.

The question of the size of the ultimate colloidal particles in starch is very difficult. By osmotic pressure measurements, average values for the weight of the particles have been calculated. They range from 77,000 to

260,000, the hydrogen atom being unity, but the real significance of the figures may be small because of the polydisperse character of the starch sols. These figures do not represent true molecular weights, as is sometimes assumed.

The true molecular weight of starch is not known, but studies of its crystal structure by means of X-rays suggest a comparatively simple unit of pattern such as $C_{12}H_{20}O_{10}$. This is in good agreement with conclusions drawn from chemical studies, in which anhydromaltose (identical in formula with the above) has been shown to be the major structural unit. The colloidal units must contain 200–1000 molecules of this size, and the X-ray experiments strongly suggest that in these particles the molecules are geometrically arranged in a regular pattern. It is probable, however, that this orderly arrangement is not equally good in all directions, as it is in a perfect crystal. Cases of this kind, involving complete orientation of the molecules in one or two directions and its absence in others are common, as we shall see, amongst the biological colloids. The existence of directions in which the natural structure is irregular helps to explain the ease with which water molecules can penetrate right through it, leading, under suitable conditions to complete peptization.

The colloidal properties of *Inulin*, which occurs as a reserve carbohydrate in many species of plants, have been little studied, but it appears to form true solutions in hot water and colloidal sols in cold water. It occurs naturally as a sol in the cell sap.

*Lichenin*, found in mosses and lichens, is chemically very closely related to cellulose, but unlike the latter readily gives sols in water.

*Glycogen.* It is well known that animals accumulate their reserves as fats rather than as carbohydrates, but nevertheless animal starch or glycogen plays an important part in physiological processes and is to be found in muscle and in the liver. It has also been isolated from fungi. In chemical reactivity and structure it bears extraordinary resemblance to starch and its colloidal properties also are similar. It has been split into two fractions —a sol rich in phosphorus (0·72 per cent. $P_2O_5$) and a precipitate poor in phosphorus (0·13 per cent. $P_2O_5$). The particle size of glycogen sols is about the same as that of starch. It differs from starch in being completely amorphous. X-ray studies have given no hint even of an approximation to a regular crystal structure.

*Cellulose.* The colloidal properties of cellulose are much less evident than those of starch. It occurs as a major structural unit in the cell walls of plants and from this material no simple means have yet been devised for the direct preparation of a cellulose sol. Such sols can only be prepared via one or other of the cellulose esters or the complex cellulose-metallic salt compounds now used so largely in the artificial silk industry. These products take the form of flocculent precipitates, devoid of microscopic structure, but showing an essentially crystalline character when examined by X-ray methods. In the plant fibres formed of cellulose, a sub-microscopic crystalline structure has, by microscopists, long been suspected of being responsible for their remarkable optical properties. These suspicions have been verified and amplified by X-ray methods, as we shall see later. But even in these fibres certain colloidal properties are present. Thus they undergo a swelling in dilute alkalis and it has been shown that this does not affect the length of the fibres but only the cross-section. One might conclude from this either that the crystalline structure along the axis of the fibre is much more perfect than that at right angles, or else, that the union of molecule to molecule across the fibre is much weaker than that along it. The actual pattern unit of cellulose is now believed to be small, consisting of three or four glucose molecules. The colloidal units from which the fibres are built up are comparatively large, probably larger and more perfectly crystalline than those of starch.

*Lignocellulose.* Very little is known either of the chemical structure or the colloidal properties of this important constituent of woody tissues. It is supposed to act as a kind of cement between adjacent cellulose fibres, thus stiffening the whole structure. It is not even certain whether lignocellulose is a true compound or an intimate mixture of cellulose and lignin. We have some information on the chemical nature of lignin, but its colloidal properties have almost completely escaped study. Its general character is that of a colloidal acid, but the acidic properties are not so marked as those of humic matter which is, as we have already seen, so largely derived from it.

**Proteins.**—More numerous, more varied in properties and more intimately concerned in the mechanism of life processes than the carbohydrates are the great nitrogenous family of the proteins. The nucleus of every living cell consists of proteins and they are present also not only as constituents of the protoplasm, but in many extracellular forms having specialized and highly important functions in animal physiology. Their classification is made on a chemical and colloidal basis, and their similarity in fundamental behaviour rests on the fact that all proteins give amino-acids when the large molecules are broken down into their simplest units. This essential similarity may be traced to the properties of these amino-acids which, by definition, contain both basic $NH_2$ groups and acids COOH groups in the molecule. The proteins reflect this dual character in their chemical and their colloidal behaviour and the word " amphoteric " has been coined to express this property of reacting both as acids and as bases.

In one respect the proteins may be contrasted with the colloidal carbohydrates. We have seen that the latter have small, identical pattern units and that the colloidal units are more or less crystalline aggregates of comparatively simple molecules. The proteins show the opposite behaviour. The molecules themselves are so large as to be justly termed colloidal. A few members of the protein family form crystals by aggregation of these large molecules, yet when examined by X-ray methods such crystals appear completely amorphous. Only in the formation of certain fibres like wool and silk can one trace some similarity of structure between the proteins of which they are built and the fibrous carbohydrate cellulose. This aspect will be taken up in the next chapter.

The molecular weights of the proteins are generally assumed to be the same as their particle weights determined by osmotic pressure measurements or by sedimentation in a high-speed centrifuge. The justification for this assumption lies chiefly in the fact that those proteins which readily disperse in water always attain the same degree of dispersion and that the particles formed are all of the same size. Some typical values for the common water-soluble proteins are given in Table IX.

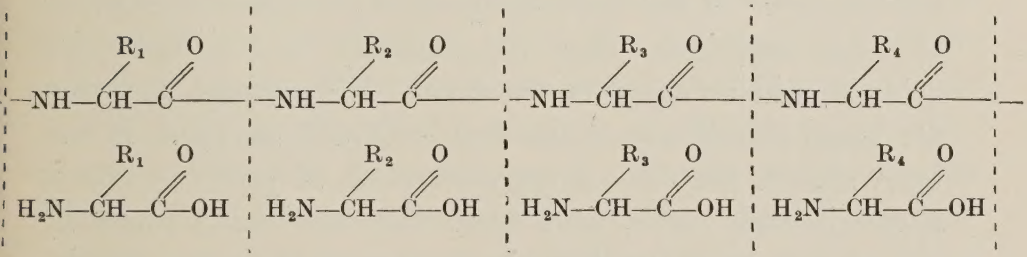
The protamines, found in the sperma of fishes have probably lower molecular weights than any of those given in the table. Their salts with acids are well-defined crystalline

TABLE IX

| Proteins. | Origin. | Molecular Weight (Osmotic). | Particle Weight (Centrifuge.) |
|---|---|---|---|
| Egg Albumin . | Hen's eggs | 34,000 | 34,500 |
| Serum albumin . | Blood | 45,000 | 66,700 |
| Serum globulin . | Blood | 80–140,000 | 104,400 |
| Hæmoglobin . | Blood | 66,800 | 68,000 |
| Gelatin . . . | Collageen of bones | 68,000 | — |

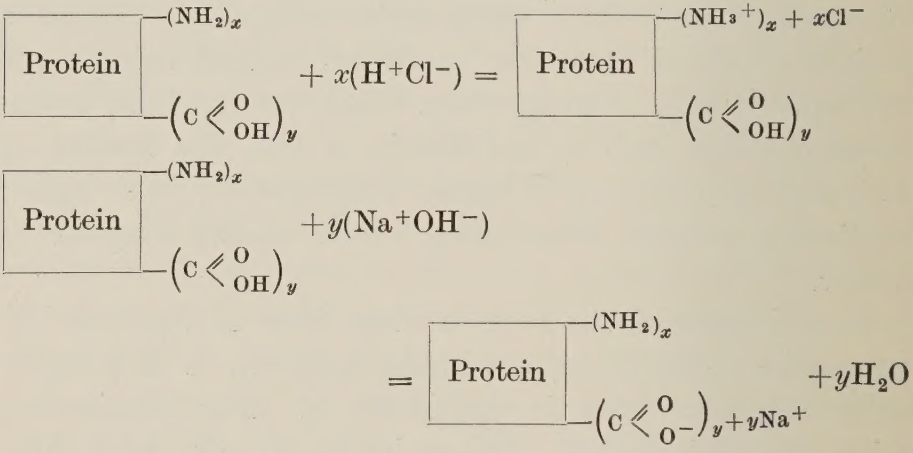
compounds and their composition suggests a formula weight of about 2000, the molecular weight being some multiple of this. On the other hand, the insoluble structural proteins such as the fibroin of silk, the keratin of hair and the collageen of leather may possibly have higher molecular weights than those which readily disperse in water.

It is impossible to form a clear idea of the colloidal properties of the proteins without reference to their molecular structure, and in particular to their relationship with the amino-acids. Below is shown part of a long chain whose recurring units are amino-acid residues. The amino-acids themselves are shown underneath :



$R_1$ $R_2$ $R_3$ and $R_4$ represent organic radicals, sometimes simple like —$CH_3$, but they may also be complex.

In the first place, it is clear that when such a chain is finally completed there will be at one end an acidic —COOH group and at the other a basic —$NH_2$ group. These will confer amphoteric properties on the protein. But other —$NH_2$ and —COOH groups may also be present in the radicals which have been denoted by $R_1$ $R_2$ $R_3$ and $R_4$, and they will undergo the same kind of reactions as the end groups. The effects of acids and bases on proteins may thus be represented diagrammatically as follows:



$$\boxed{\text{Protein}}\begin{matrix}-(NH_2)_x\\ \\ -\left(C{<}^{O}_{OH}\right)_y\end{matrix} + x(H^+Cl^-) = \boxed{\text{Protein}}\begin{matrix}-(NH_3{}^+)_x + xCl^-\\ \\ -\left(C{<}^{O}_{OH}\right)_y\end{matrix}$$

$$\boxed{\text{Protein}}\begin{matrix}-(NH_2)_x\\ \\ -\left(C{<}^{O}_{OH}\right)_y\end{matrix} + y(Na^+OH^-)$$

$$= \boxed{\text{Protein}}\begin{matrix}-(NH_2)_x\\ \\ -\left(C{<}^{O}_{O^-}\right)_y + yNa^+\end{matrix} + yH_2O$$

In each case the effect is that a molecule originally neutral acquires a positive or a negative charge, together with the accompanying ionic atmosphere which balances this charge. If this indeed represents the true mechanism of these reactions, then the capacity to combine with acids should be equal to the free —$NH_2$ groups and that for bases should equal the free —COOH groups. It has been shown that for a large number of proteins this is approximately true, and that the combining capacity ranges from 30–200 milliequivalents per 100 grams protein.

In any given protein the numbers of —$NH_2$ groups and —COOH groups are usually different; furthermore, their strengths as determined by their tendency towards ion formation are not alike. Hence the attraction for hydrogen ions will, in general, be different from that for hydroxyl ions. It will therefore be exceptional for the neutral point of water (where the hydrogen and hydroxyl ion concentrations are equal) to coincide with the point at which the protein is un-ionized. This point of minimum ionization is called the *isoelectric point* and at this point the protein will travel neither to the positive nor the negative pole when an electric current is applied. If the acidic groups predominate, then the isoelectric point will be on the acid side of the neutral point ($p\mathrm{H} < 7$); if the basic groups predominate it will be on the alkaline side of the neutral point ($p\mathrm{H} > 7$). Table X gives some illustrative examples.

TABLE X

| Protein. | Character. | *p*H at Isoelectric Point. |
|---|---|---|
| Egg albumin . . | Acid | 4·6 |
| Serum albumin . | Acid | 5·0 |
| Serum globulin . | Acid | 4·4 |
| Hæmoglobin . . | Very slightly acid | 6·8 |
| Gelatin . . . . | Acid | 4·7–5·2 |
| Histone . . . | Alkaline | 8·5 |
| Protamine . . . | Alkaline | 12·0 |

Now the conditions governing the dissociation into ions of amphoteric substances are quite different from those already discussed in connection with colloidal acids. Consider neighbouring acid and basic groups at the isoelectric point. The former attempt to surround themselves with an ionic atmosphere of hydrogen ions, the latter with one of hydroxyl ions. But hydrogen and hydroxyl ions have an intense attraction for one another, so much so that in pure water only one of each are simultaneously present in ten million water molecules. Hence if acid and basic groups are both present it is impossible for either to be highly dissociated, in fact, compared with free acids and bases they must be very weak indeed.

The weakness of the acid and basic groups in the proteins is reflected in the properties of both types of salts. Each is only stable for suitable values of the hydrogen or hydroxyl ion concentrations. Thus if, for instance, gelatin chloride is prepared by adding dilute hydrochloric acid to isoelectric gelatin, then the salt formation is only complete in presence of a distinct excess of hydrochloric acid. If this is washed out the salt splits up once more into gelatin and hydrochloric acid. It is this ready reversal of the salt-forming reactions which masks other processes such as cation and anion exchange reactions and makes these last of subordinate importance in the colloid chemistry of the proteins.

The salts produced by the action of relatively strong acids and bases on proteins are ionized to a considerable extent. Their colloidal properties may be summarized in the statement that they are much more highly hydrated than the isoelectric protein. It is this effect which is responsible for the enhanced swelling of proteins in dilute acids and alkalis. At the isoelectric point the water-imbibing capacity is at a minimum, the electric charge is zero and the tendency towards coagulation is at a maximum. When salt formation is just complete the water held is at a maximum, the electric charge is at a maximum and the tendency towards coagulation is at a minimum.

The coagulation of proteins by salts is largely controlled by their hydrophile character, and only in a few instances where the hydration is small do we find the same kind of regularities as for the hydrophobe sols. In general, very high concentrations are required for complete coagulation and the order of effectiveness is that of the hydration of the salts used. Here we can regard the proteins as being in competition with the salt for the available water. When the salt is able to take water from the hydrated protein coagulation occurs. In some cases it is not possible to coagulate proteins by salts. The class known as the globulins is actually dispersed by moderate concentrations of salts and is characterized by this fact.

The characteristic of the albumin group of the proteins is their coagulation by heat. It is typified in the setting of egg white on boiling and in the formation of an insoluble skin of lactalbumin on the surface of boiled milk. This irreversible coagulation is very imperfectly understood. It is possible, indeed, that it is an intramolecular change and that a new molecule, less hydrated than the original, is formed.

The range of hydration values within the protein family is enormous. On the one hand we have the soluble protamines and at the other extreme the proteins of hair, of sponges, of horn and of feathers which do not give colloidal sols at all and which only take up water to a limited extent, whilst retaining their inherent structure.

The proteins are not only an important class in themselves but they combine with other types of molecules to form a class of conjugated proteins. Here are to be found some of the most important constituents of living cells; the nucleo-proteins from the nuclei of cells, the lecitho-proteins of the cytoplasm and chromoproteins such as the hæmoglobin of blood corpuscles. These con-

TABLE XI

| Type. | Group. | Group Characteristics. | Examples. | Remarks. |
|---|---|---|---|---|
| Simple | Albumins | Soluble in water<br>Coagulated by heat | Ovalbumin<br>Lactalbumin | From egg white.<br>From milk. |
| ,, | Globulins | Insoluble in water. Peptized by salt solutions | Ovoglobulin<br>Edestin<br>Fibrinogen | From egg yolk.<br>From hemp seed.<br>From blood. |
| ,, | Glutelins | Insoluble in water and salts. Soluble in acids and bases | Glutenin<br>Oryzein | From wheat.<br>From rice. |
| ,, | Prolamins (or Gliadins) | Soluble only in 70–80 per cent. alcohol | Gliadin<br>Hordein | From wheat.<br>From barley. |
| ,, | Scleroproteins (or albuminoids) | Insoluble in above reagents | Keratin<br>Collageen | From hair and feathers.<br>From tendons, bones, etc. (gives gelatin on boiling with water). |
| ,, | Histones | Insoluble in water or in dilute ammonia. Soluble in dilute acids. Basic | Globin | From hæmoglobin. |
| ,, | Protamines | Soluble. Highly basic | Salmin<br>Sturin | From salmon sperm.<br>From sturgeon sperm. |
| Intermediate | Phospho-proteins | Contain phosphoric acid | Caseinogen<br>Vitellin | From milk.<br>From egg yolk. |
| Conjugated | Nucleo-proteins | Protein + nucleic acid | Nuclein<br>Nucleohistone | From glandular tissues.<br>From yeast. |
| ,, | Gluco-proteins | Protein + carbohydrate | Mucin | From salivary glands and jellyfish. |
| ,, | Chromo-proteins | Protein + coloured molecule | Hæmoglobin | From red blood corpuscles. |
|  | Lecitho-proteins | Protein + lecithin |  | From cytoplasm. |

jugated proteins still display the characteristic salt formation with acids and bases but, in addition, the non-protein part of the molecule introduces fresh reactions of its own.

The relationships within the protein family can perhaps most simply be appreciated if the classification is tabulated. It will be seen from Table XI that the colloidal characters are relied upon to a considerable extent in separating the groups.

### SUPPLEMENTARY READING

R. Zsigmondy's *Kolloidchemie*, Vol. 2 (Leipzig, 1925) and W. Pauli and Volko's *Elektrochemie der Kolloide* (Wien, 1929) both devote separate sections to the colloidal properties of carbohydrates and proteins. On the biological side R. A. Gortner's *Outlines of Biochemistry* (New York, 1929) gives a full account of the proteins and E. C. Miller's *Plant Physiology* (New York, 1931) should be referred to for a critical account of the functions of carbohydrates and the proteins in plant life. The following monographs are also available: P. Karrer, *Die Polymere Kohlehydrate* (Leipzig, 1925); H. Pringsheim, *Die Polysaccharide* (Leipzig, 1931); T. B. Robertson, *The Physical Properties of the Proteins* (London, 1918); J. Loeb, *Proteins and the Theory of Colloidal Behaviour* (New York, 1924).

## CHAPTER XII

# COLLOIDAL ARCHITECTURE IN BIOLOGICAL STRUCTURES

In the chemical and physical study of natural products two surprising sets of observations have frequently been commented on. One set includes all those instances of gel formation in which quantities of the order of 1 per cent. solid material are able to form rigid gels with 99 per cent. or thereabouts of pure water. The other set is concerned with the remarkable strengths of natural fibres. It is only within recent years that these facts have received adequate explanation, and since in each case this involves both the shape of the colloidal units and their arrangement, they have been grouped here under the general heading of colloidal architecture.

**The Structure of Gels.**—In seeking to explain the high water content of many comparatively rigid gels it was soon realized that purely chemical forces were inadequate ; that although a high degree of chemical hydration operates as a favourable circumstance in gel formation, the shape and arrangement of the colloidal particles themselves frequently overshadow it in importance. It has often been suggested that gels attain simultaneously a high rigidity and a high water content by means of a honeycomb or sponge-like framework. This conclusion is not upheld by modern workers, who regard the most common type as a felt-like structure in which the liquid is enmeshed between a multitude of irregular, interlacing fibres or threads. Such fibres may originate in various ways. In the proteins and colloidal carbohydrates there is little doubt that the molecules themselves are in the form of long chains and that they aggregate together to give fibrous or rod-shaped colloidal units. In other cases the molecules themselves may have similar dimensions in all directions and yet may, by crystallization, produce long needle-shaped particles. There remains another mechanism whereby a felt-like structure can be produced, even from spherical particles. It has been shown that in the region of slow coagulation, where only a fraction of the collisions between particles are effective there is a much greater chance of aggregation into chains than into compact clusters. As this process continues, these ever-branching chains eventually link up throughout the whole system, thus imparting to it a comparatively high rigidity. Although we are still unable to say with certainty which mechanism operates in the case, for example, of the jellyfish (with less than 1 per cent. of dry matter), or in that of the grown tadpole (with exactly 1 per cent. of dry matter), their comparatively high rigidity is no longer so complete a mystery.

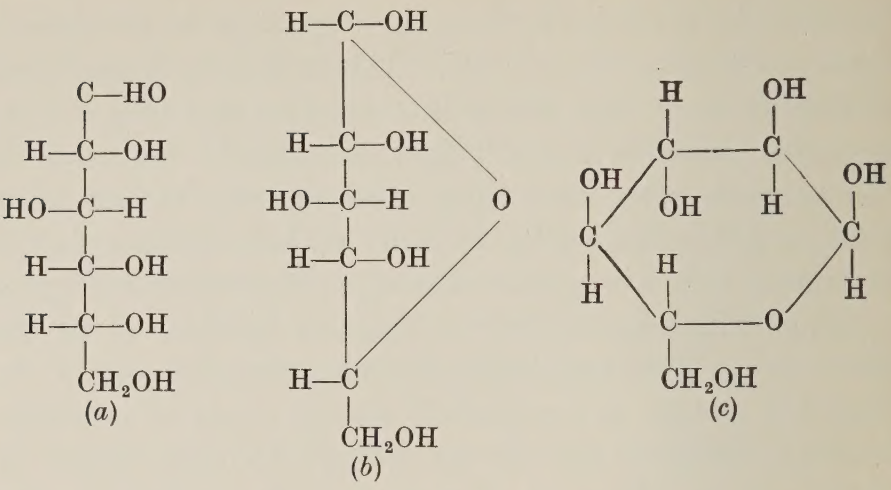
**The Structure of Natural Fibres.**—Within recent years one of the most fruitful fields of collaboration between physicists and chemists has been in the study of fibrous biological structures. It is worth while considering how this has come about. The organic chemist has acquired a reasonably exact knowledge of the molecular fragments from which the complete molecules of cotton cellulose, silk fibroin, wool keratin and so on are built up. The physicist for his part has studied closely such properties of the whole fibres as their mechanical strength and their moisture-absorbing capacity, which are of direct importance in the textile industries. These studies led to an acknowledgment that fibres are structures built of colloidal units whose sizes could sometimes be roughly estimated from the physical properties. The great gap between these physical units and the molecular fragments of the organic chemist has recently been bridged by X-ray methods, so that it is now possible to show how the chemical structure determines the more outstanding physical properties.

It may be recalled that the study of the diffraction of X-rays by perfect crystals has led, in many cases, to a complete determination of the geometrical arrangement of the atoms present. Nothing so comprehensive is possible with fibres. The experiments show merely that certain regular spacings, having a definite geometrical relationship to the fibre axis, are present. These spacings enable one to calculate the size and shape of the unit of pattern, which by repetition gives the complete fibre. This unit of pattern is not necessarily a molecule. It may be only a part of a complete molecule, or it may consist of several. Now in the case of the natural fibres the spacings are comparable in size with the molecular fragments of the organic chemist, the exact sizes of which are already known from other measurements. These fragments can now be fitted together so that they will give the spacings found by X-ray measurements, and the arrangement so adopted can be taken as typical of the whole fibre.

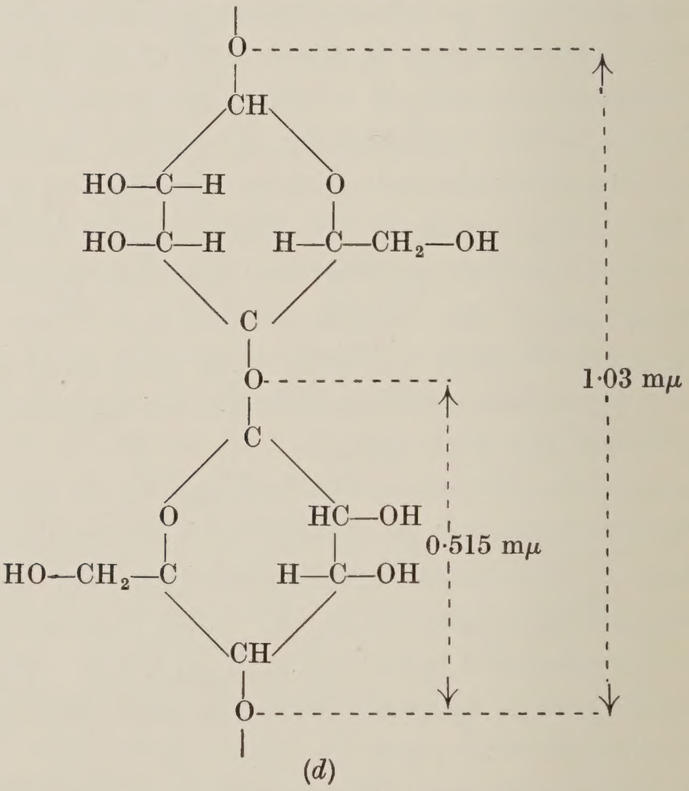
*Cellulose.* Although cellulose samples from different plants give X-ray diffraction diagrams of varying degrees of perfection, the fundamental spacings are always the same. Since cellulose is made up entirely of glucose units it should be possible to relate these spacings to the dimensions of the glucose molecule. This is usually represented as having six carbon atoms in a straight line (Fig. 12 (*a*) and (*b*)), whereas actually it is hexagonal, one atom of the hexagon being an oxygen atom and one carbon atom forming a side chain (Fig. 12 (*c*)). A chain of these glucose hexagons linked together through oxygen atoms gives spacings which correspond to those of cellulose along the fibre axis. The cellulose molecule, therefore, may be regarded simply as a repeating glucose chain of indefinite length. Neighbouring chains adhere to each other by their residual chemical affinity; not by definite bonds such as are found along the chains. It will be seen from Fig. 12 (*d*) that prominent spacings are 0·515 m$\mu$ and 1·30 m$\mu$ corresponding to the length of one and two glucose residues respectively. These are actually present in cellulose and are prominently shown by the diffraction effects. In the colloidal units of the fibre it is believed that the chains are over 100 glucose units long, that is, over 50 m$\mu$, and that possibly 100 chains lie parallel, giving the diameter of the bundle as 5–6 m$\mu$. The size and arrangement of these colloidal units may vary according to the origin of the cellulose. In cotton they form a steep spiral round the fibre axis.

The use of cellulose in the building up of the cell wall has been investigated in the case of a green alga, *Valonia ventricosa*. Here have been found two sets of cellulose chains making angles of 60–80° with one another, the chains lying parallel to the cell wall (Fig. 13). This affords an instance of a fibrous unit being used to build up a lamellar structure.

The remarkable strength of cellulose fibres is due to the way in which the needle-shaped colloidal units are associ-



(*a*) Aldehyde formula for glucose.
(*b*) ∂-Lactone formula for glucose.
(*c*) ∂-Lactone formula arranged spatially



(*d*) Glucose units in the cellulose chain.

FIG. 12.

ated. The breaks in the long parallel chains occur at random, just as they do in a spun thread and, indeed, a single cellulose fibre may be regarded as a thread spun from the colloidal units. Its true elasticity operates over a short range only. Greater extensions cause a permanent increase in length, which is ascribed to the long colloidal units slipping over one another under load. This irreversible type of extension quickly leads to breakage.

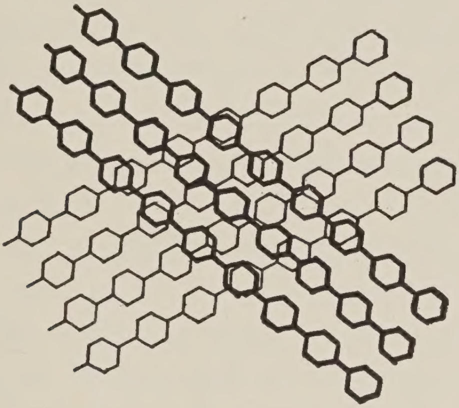
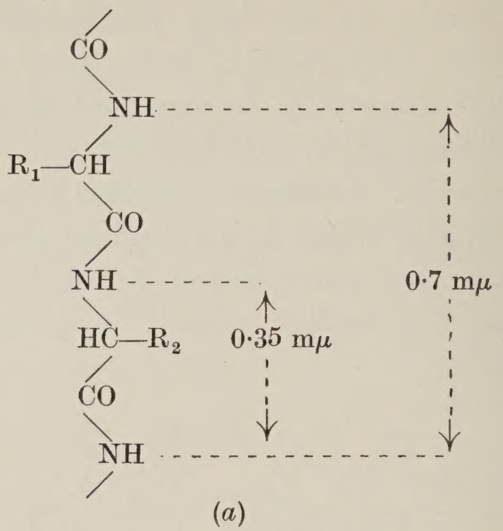
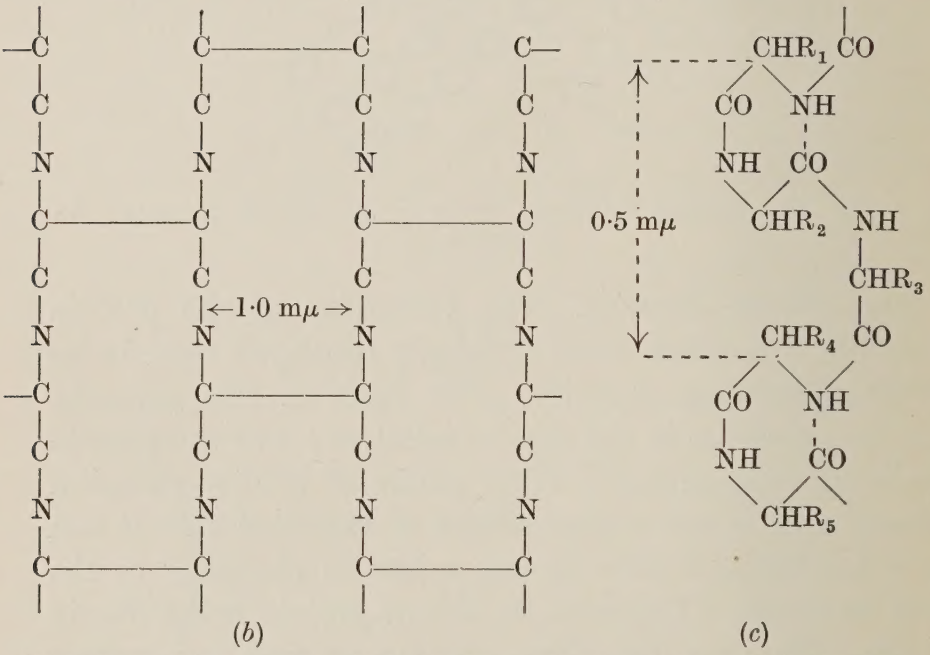


FIG. 13.—Crossed Cellulose Chains in the wall of *Valonia ventricosa.*

*The Fibrous Proteins.* The versatility of the protein molecule is nowhere more strikingly displayed than in its structure-building capacity. The basis of this property is a long chain as in the case of cellulose ; but the protein chain contains so many more points of intense chemical affinity and so many possibilities of variation that it can do other things besides giving a fibrous character to the final structure. The simplest fibrous protein is the fibroin of silk. Here the diffraction spacings are easy to interpret once a model of the chain is set up (Fig. 14 (*a*)). It should be noted that although the chain appears zigzag it is really in its fully extended state. The angles are fixed in advance


CO
NH
R₁—CH
CO
NH
HC—R₂
CO
NH
0·7 mμ
0·35 mμ
(a)

(*a*) Portion of a fully-extended protein chain. Each amino-acid residue contributes 0·35 mμ to the length.


C
N
←1·0 mμ→
0·5 mμ
CHR₁ CO
CO NH
NH CO
CHR₂ NH
CHR₃
CHR₄ CO
CO NH
NH CO
CHR₅
(b)
(c)

(*b*) Linkages between protein chains forming a network at right-angles to the plane of (*a*).

(*c*) A folded protein chain. The spacing 0·5 mμ becomes 1·02 mμ, i.e. 3 × 3·5 mμ when fully stretched as in (*a*).

Fig. 14.

by the arrangement in space of the four bonds of the carbon atoms, which make equal angles of 109° 28′ with one another. The adherence of neighbouring chains to each other is even stronger than in the case of cellulose, because the —NH— and $>C=O$ groups are intense centres of chemical affinity. This strong lateral adhesion makes silk stronger than cotton by hindering the slipping of one chain over another. The X-ray diffraction photographs of silk show a pronounced spacing of 0·35 m$\mu$ along the fibre axis which agrees with the length of the repeating —N—C—C— sequence in the chain (Fig. 14 (*a*)). Other spacings indicate that the total width including the side chains is about 1·0 m$\mu$ and the front to back value is 0·46 m$\mu$.

In contrast to silk, wool and mammalian hair show a very poor diffraction and the spacings deduced from this seem, at first sight, to have no connection with the protein chain. Now wool and hair have remarkable elastic properties. In the moist state particularly they show up to 100 per cent. extension under load, yet spring back to the original length when the load is removed. This enormous elasticity is found to be a property of the protein chain itself, for if the stretched hair is examined by the X-ray method it yields quite different spacings from those of the unstretched hair. Moreover, in the extended hair the spacings are practically the same as those of silk fibroin. In wool and hair, therefore, the protein chain is like a spring ; under normal circumstances it is in a folded state ; when stretched, the chain is straightened out but still acted upon by forces which can pull it back into the folded condition when the extending force is removed. Under certain circumstances, indeed, it contracts beyond the original length. What kind of molecular picture can be drawn to account for these facts and for the observed spacings ? Now in keratin, the protein of wool and hair, there is good chemical evidence that the parallel protein chains are joined together at various points by side chains containing sulphur atoms. In the plane of the side chains we therefore have a net-like structure, which in the stretched condition would resemble Fig. 14 (*b*). The colloidal units may be considered to be built up by an array of such nets, one behind the other, like fishing-nets hung out to dry. In the folded state the nets are crumpled in long folds parallel to the side chains (Fig. 14 (*c*)). It is supposed that the mechanism of this folding lies in the attraction of a $>C=O$ group for an —NH— group of the same chain, a hexagonal arrangement being finally attained. The calculated spacing for this agrees very well with the chief spacing of unstretched wool.

The colloidal properties of wool have been studied in some detail. It has been shown that the swelling in water, which chiefly affects the cross-section, takes place by absorption between the colloidal units. As swelling occurs, therefore, the channels in the wool structure become larger, reaching eventually a diameter of about 4 m$\mu$. In dry wool the corresponding dimension is only 0·6 m$\mu$. The colloidal units from which the fibre is constructed are assumed (in agreement with the X-ray evidence) to consist of thin plates like laths considerably longer than broad. Their thickness has been calculated to be about 20 m$\mu$, the length is at least ten times as great, and the breadth remains, as yet, undetermined.

It is an interesting and significant fact that the protein of muscle, known as myosin, gives spacings very similar to those of unstretched hair or wool. It is therefore in the form of a folded protein chain and it is suggested that the contraction of muscle is analogous to that of wool.

The special ease with which muscle contracts is probably a reflection of the detailed structure of its own folded protein chain. An example of greater and more permanent folding of the main chain is afforded by collageen (from hide, etc.) and also by the gelatin derived from it. What was a 0·35 m$\mu$ spacing in fibroin has now diminished to 0·28 m$\mu$. A less complete folding of the protein chain, giving a spacing of 0·31 m$\mu$, is suggested for the keratin of feathers. Other examples of biological importance are continually being added to this list of structures whose main features can be elucidated by the new X-ray technique.

## Supplementary Reading

The only work which summarizes all the recent developments in the elucidation of fibre structures is W. T. Astbury's *The Fundamentals of Fibre Structure* (London, 1932).

## CHAPTER XIII

# MILK AND MILK PRODUCTS AS COLLOIDAL SYSTEMS

It is doubtless no accident that in the milk of all the mammals a high percentage of the actual food forms part of a colloidal system. The advantages of such an arrangement are plain. Since the food must be transferred from the adult to the infant a liquid medium provides the most economical and satisfactory means by which it can be done. In this way the requirements of the young animal for water and mineral substances can be met along with its need for body builders and energy providers. Now one conceivable means of achieving this would be by the use of a true solution of comparatively simple organic compounds, but it is open to two serious objections. Firstly, such a liquid would have a very high osmotic pressure, causing grave difficulties in production. Secondly, it would bear no resemblance to the food with which the young animal would have to deal in later life. Actually, milk provides the young animal with one part of its requirements in true solution (milk sugar), another part as a colloidal sol (the proteins), and the third part as an emulsion of microscopic droplets of oil (the butter-fat).

**The Butter-Fat Emulsion.**—Although most of the butter-fat globules in milk are too large for the description colloidal yet their properties and reactions are to a large extent determined by what happens at the water-oil interface. Amongst the mammals there is considerable variation in the mean size of the fat particles, those of cow's milk being larger than those of goat's, sheep's or human milk. As we are concerned mainly with cow's milk it is worth while considering the actual distribution of particle sizes and the factors which influence the size. Table XII gives figures illustrating differences between breeds of cattle and changes in particle size during lactation. It is found that the mean particle size increases in the series Holstein $<$ Ayrshire $<$ Shorthorn $<$ Jersey.

## TABLE XII

(M. H. Campbell's Data)

THE SIZE DISTRIBUTION OF FAT GLOBULES IN COW'S MILK

| Fraction. | Holstein. | | Guernsey. | |
|---|---|---|---|---|
| | 2nd Month of Lact. | 10th Month of Lact. | 3rd Month of Lact. | 10th Month of Lact. |
| | Per cent. | Per cent. | Per cent. | Per cent. |
| 0·5– 1·5 $\mu$ | 32·2 | 48·9 | 23·4 | 29·5 |
| 1·5– 2·5 $\mu$ | 25·7 | 31·0 | 23·9 | 31·8 |
| 2·5– 3·5 $\mu$ | 18·7 | 14·6 | 21·3 | 23·3 |
| 3·5– 4·5 $\mu$ | 12·5 | 4·2 | 15·8 | 9·4 |
| 4·5– 5·5 $\mu$ | 7·2 | 1·1 | 9·4 | 4·1 |
| 5·5– 6·5 $\mu$ | 2·8 | 0·2 | 4·4 | 1·4 |
| 6·5– 7·5 $\mu$ | 0·8 | 0·03 | 1·6 | 0·3 |
| 7·5– 8·5 $\mu$ | 0·1 | 0·00 | 0·2 | 0·1 |
| 8·5– 9·5 $\mu$ | 0·0 | 0·00 | 0·1 | 0·04 |
| 9·5–10·5 $\mu$ | 0·03 | 0·00 | 0·05 | 0·03 |
| Mean volume | 17·8 $\mu^3$ | 6·0 $\mu^3$ | 24·7 $\mu^3$ | 13·4 $\mu^3$ |
| Mean diameter | 3·2 $\mu$ | 2·3 $\mu$ | 3·6 $\mu$ | 3·0 $\mu$ |

During a lactation period there is a distinct tendency for the average size to decrease with time. Feeding experiments have shown no clear connection between the diet and the size of the butter fat globules.

The actual number of fat globules in each cubic centimetre of milk will depend both on the total butter-fat content and on the particle size distribution. The values range around $3 \times 10^9$ particles per c.c. It will be noticed that Table XII gives no particulars of fat globules smaller than $0{\cdot}5\,\mu$. Such particles are present only in very small amount. On the other hand, homogenized milk contains practically the whole of the fat in the form of globules less than $1\,\mu$. The total number of particles is increased about one thousandfold and the mean diameter is correspondingly reduced to about $0{\cdot}3\,\mu$, one-tenth of its value for normal milk.

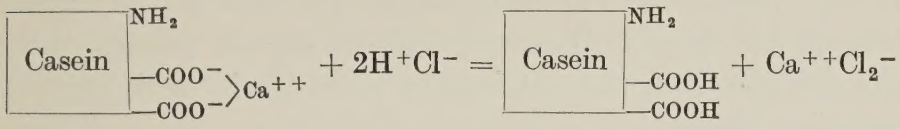
The rise of the butter-fat globules to form a cream layer is one of the most intensively studied properties of milk. In Table I, Chapter III, the calculated times for 1 cm. rise have already been given, taking various diameters for the particles. Here particles of $5\,\mu$ diameter should rise 1 cm. in about 4 hours. Now the speeds calculated from the dimensions of the individual particles are very much less than the rate of formation of a cream layer would indicate. Hence it may be concluded that the particles are not moving wholly as individuals. In other words, we are dealing either with a coagulating or a coagulated system. Now the microscopic examination of samples freshly drawn from the cow shows that the fat globules are present as individuals; they aggregate together on standing. Hence the system is coagulating; but the slow rate of rise and the ease with which the aggregates are broken up by shaking would seem to indicate that we are in the region of slow coagulation. The aggregates formed are not compact, they behave as though they contain rather less than 50 per cent. of butter fat, and the cream layer initially formed from them has only 20–30 per cent. of fat. When centrifugal force is used instead of gravity a much greater fat content is attainable, due to a closer packing of the individual fat globules. In fresh cream the coagulation has not caused actual union of the globules ; slight mechanical shaking is sufficient to redisperse them. On the other hand, violent and prolonged shaking does cause union, leading to the formation of butter. We shall discuss this churning process later.

It was realized at an early date in these investigations that the adhesion of fat globules without actual coalescence called for some special explanation. It was suggested that they are surrounded by a membrane of protein material ; we now describe it as an adsorbed layer of protein. There is a good chemical evidence in support of this theory. Cream can be repeatedly washed with distilled water without removing all the nitrogenous substances, and the most recent work along these lines strongly suggests that this adsorbed layer is a mixture of about 80 per cent. of protein and some 20 per cent. of a lecithin-like substance containing phosphorus. Measurements of the speed of movement of the fat globules in an electric field show clearly that they behave as large protein particles, that is to say, the thin layer of adsorbed protein completely dominates the surface reactions. It acts as a protective colloid, but in a somewhat restricted sense. For this protein layer is actually more sensitive to certain coagulating agents than the fat globule itself, as is clearly shown by the effect of adding acid. A fat globule in pure water only loses its negative charge at a concentration of about

$\frac{N}{200}$ acid. When "protected" by the protein layer the electric charge is zero for $\frac{N}{10,000}$ acid, due to the fact that at this concentration the protein itself is isoelectric. Hence, although the protein layer prevents coalescence, it sensitizes the fat globules towards coagulating agents acting on the acid side of the neutral point.

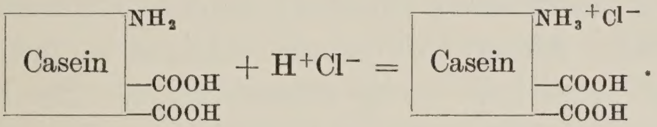
Butter fat melts at about 29–33° C. and one would therefore expect that in milk kept at ordinary room temperature the fat globules would be solid. This is not necessarily the case. The globules are composed of a mixture of fats and such mixtures are notoriously prone to supercooling; that is, remaining liquid at temperatures below the true melting-point. This tendency to supercooling is much accentuated by the small size of the globules and by the fact that the adsorbed layer of protein keeps the individuals apart. Some globules might therefore be solid while others were still liquid, but as soon as such mixed globules were made to coalesce, the whole mass would instantly become solid, since supercooled liquids immediately crystallize when a trace of the solid is added.

**The Casein Sol.**—The major protein constituent of milk is casein, often referred to as caseinogen, because in actual fact the calcium salt of the protein casein is associated with calcium phosphate. From this mixture the protein itself is readily prepared by precipitation with dilute acid. This does two things. It removes the calcium phosphate by bringing it into true solution and it also liberates calcium from the calcium caseinate. This precipitation is, as one would expect, only complete at the isoelectric point of casein, which occurs well on the acid side of the neutral point (*p*H 4·7). The reaction can be represented :



$$\boxed{\text{Casein}}\begin{array}{l}\text{NH}_2\\ \left.\begin{array}{l}\text{—COO}^-\\ \text{—COO}^-\end{array}\right\rangle \text{Ca}^{++}\end{array} + 2\text{H}^+\text{Cl}^- = \boxed{\text{Casein}}\begin{array}{l}\text{NH}_2\\ \text{—COOH}\\ \text{—COOH}\end{array} + \text{Ca}^{++}\text{Cl}_2{}^-$$

A further quantity of acid brings the protein back into solution by formation of a salt thus :



$$\boxed{\text{Casein}}\begin{array}{l}\text{NH}_2\\ \text{—COOH}\\ \text{—COOH}\end{array} + \text{H}^+\text{Cl}^- = \boxed{\text{Casein}}\begin{array}{l}\text{NH}_3{}^+\text{Cl}^-\\ \text{—COOH}\\ \text{—COOH}\end{array} .$$

This second reaction illustrates the basic character of the protein, but the fact that the isoelectric point occurs so markedly on the acid side of neutrality indicates that the acid character is much stronger than the basic. Casein, indeed, has an appreciable strength as an acid. It can even liberate carbon dioxide from carbonates. Its sodium, potassium and ammonium salts are all highly dispersed in water. Their solutions give osmotic pressures which correspond to a molecular weight of about 33,000 for casein. The ultracentrifuge gives higher values, about 98,000, which would imply particles about 5 m$\mu$ in diameter.

The caseinogen particles present in milk are much larger than this. They can be readily observed in the ultramicroscope and their size has been estimated at 150–200 m$\mu$. Cow's milk contains about $6 \times 10^{12}$ such particles per c.c. In human milk they are noticeably smaller, but are still visible in the ultramicroscope.

Slight changes in the composition of the outer liquid have a great influence on the size of the caseinogen particles. Souring causes a sudden coagulation and clotting as soon as the isoelectric point of casein is approached. On the other hand, addition of sodium chloride disperses the particles to such an extent that none are visible in the ultramicroscope. This is probably due to a partial formation of the highly dispersed sodium salt of casein. Like the fat globules, the caseinogen particles in milk carry a negative charge.

The association of the calcium caseinate with calcium phosphate in caseinogen has been studied in some detail. It is improbable that a chemical compound of fixed formula is present. About half of the calcium in milk can be removed by dialysis or by ultrafiltration. The boiling of milk causes a close association between the protein and the calcium, so that less passes through the membrane on dialysis.

**Other Colloids of Milk.**—The only other colloid whose presence in milk is readily detected is lactalbumin, although small amounts of two other proteins, lactoglobulin and an alcohol-soluble protein, also occur. Lecithin, which is the glycerophosphate of a nitrogenous base, is also present in small amount. The micro-organisms too cannot be omitted from a complete list, since in sour samples as many as $10^8$ per c.c. may be found, although their total weight is small.

Lactalbumin has properties very similar to those of serum albumin from blood. It is coagulated when milk is heated and forms, along with some casein and fat carried to the surface, the well-known skin on boiled milk. This change, characteristic of the albumins, is probably a molecular reaction and not merely a coagulation in the purely colloidal sense. The albumins form very highly dispersed colloidal systems, whose particles have been estimated to have molecular weights of about 60,000–70,000.

Human milk contains rather more lactalbumin and considerably less casein than cow's milk. Average figures are: Casein, cow's milk 3·0 per cent.; human milk 1·0 per cent.; Lactalbumin, cow's milk 0·5 per cent.; human milk 0·6 per cent. Colostrum contains a very high proportion of lactalbumin, hence its power of curdling on heating. The percentage of lactalbumin may be as high as 20, but is normally 10–15 and it rapidly falls to the value for normal milk the week following calving.

It is interesting to note that the variability in amount of the constituents of milk shows a marked falling off as the degree of dispersion increases. The butter fat, which forms the largest particles, is the most variable in amount, the normal range being 2–6 per cent with occasional samples even beyond these limits. The proteins are much less variable with a range 3–4·5 per cent. Finally the substances in true solution are so constant that the freezing-point depression of milk lies normally between the narrow limits 0·545–0·565° C. The total number of colloidal particles in milk is so small compared with the number of molecules in true solution (chiefly lactose) that even extreme variations in their number can only have a negligible influence on the osmotic pressure and hence on the freezing-point depression. Milk adulterated with water can thus easily be detected by its abnormally low F.P. depression.

**Butter and Butter-Making.**—The colloid chemistry of butter-making affords one of the most striking examples of a highly developed technical process whose fundamental principles are still not understood. A great deal of research has been devoted to the subject and the main facts are now quite firmly established, yet one crucial question remains unanswered. Cream, as we have seen, is an emulsion of "protected" fat globules which are dispersed in the milk serum. In butter, on the other hand, the fat forms the continuous phase and droplets of milk serum are dispersed in it. Compared with cream it represents what we describe as an inverted emulsion. It is the exact mechanism of this " inversion " of the cream in butter-making which we are still unable to formulate with any certainty.

Such inversions have frequently been observed in the case of simple emulsions of the oil in water type, and for these certain limiting conditions have been found to operate. In the first place, the volume of the two phases must be of the same order. It would be impossible, for instance, for a 10 per cent. emulsion of oil droplets in water to invert giving a 90 per cent. emulsion of water droplets in oil. Secondly, some third substance must be present. It may either be a substance which dissolves in water or in oil and which is strongly adsorbed at the interface, or it may be a solid which readily disperses in water or in oil. The soaps afford a good example of stabilizers which act by adsorption at the interface. Sodium, potassium and ammonium soaps are soluble in water and stabilize emulsions of the oil in water type. Calcium, barium and lead soaps are soluble in oil and stabilize emulsions of the water in oil type. Provided the volumes of oil and water are comparable, it is possible to " invert " an emulsion of oil in water stabilized by a sodium soap, by the addition of a calcium salt. This converts the water-soluble sodium soap into the insoluble calcium soap, which then dissolves in the oil. The first action is therefore a " breaking " of the emulsion into two layers. Subsequent agitation then causes the " inversion " into the new water in oil type, stabilized by the calcium soap.

In the churning of cream a large number of circumstances affect the rate of its conversion into butter, but it is impossible to single out any one of them and to say that the actual inversion process is completely controlled thereby. Thus the acidity or "ripeness" of the cream, its temperature, the speed of churning and the addition of substances such as salt all affect the efficiency of the butter-making process. Yet even when most of these factors are unfavourable, butter can still be produced. It has been shown that perfectly fresh cream can be churned and so also, can cream which has been completely washed free from the milk serum. On the other hand, homogenized cream cannot be churned, but unfortunately we have no information regarding the minimum size of particle which can give butter. During the churning process the adsorbed layer of protein material on the fat globules passes into the buttermilk. No adsorbed layer has been discovered on the water globules in butter.

It is, indeed, somewhat doubtful whether butter should be regarded as an inverted emulsion in the ordinary sense. When butter is melted it immediately separates into two layers, so that its stability is dependent on the fat remaining solid. This suggests that the retention of the water is purely mechanical; that in churning, the fat globules coalesce, not into larger compact globules but into aggregates which enclose some of the buttermilk. Part of this is removed during the working up of the butter and some 13 per cent. remains. The number of water globules in butter has been estimated at $3–13 \times 10^6$ per c.c. On the average, therefore, they are larger than the fat globules in milk and all sizes from $1\ \mu$ to $50\ \mu$ have been observed.

Various theories of the churning process have been brought forward, but none will bear critical examination. It would only be confusing to enumerate them here.

**Cheese and Cheese-Making.**—Much less is known of the colloid chemistry of cheese-making than of that of butter-making. The essential reaction in cheese-making is a precipitation of the casein. This may be brought about in two ways, either by a souring of the milk until sufficient lactic acid has been produced to bring the casein to its isoelectric point, or more commonly by the action of an enzyme, rennet. The precipitated casein carries down with it the butter fat. The precise mechanism of the action of rennet is obscure. It is known that it is only effective in neutral or acid solution and that soluble calcium salts must be present. Boiled milk can only be coagulated by rennet after addition of a calcium salt. The action of the enzyme is not merely physical. About 6 per cent. of the casein passes into solution as a caseose, which, presumably, is a fragment split off from the casein molecule. The curd protein is therefore termed paracasein to distinguish it from the casein precipitated by acids, but the two are chemically almost identical. It has been shown that paracasein has a greater combining capacity for bases than casein. Nothing appears to be known as to the degree of dispersion of the butter-fat globules in the curd or in the ripened cheese.

## Supplementary Reading

Two works by R. Clayton contain important sections on the colloidal aspects of dairying, *The Colloid Chemistry of Foods* (London, 1928) and *Emulsions* (London, 1928). He has a summarizing article "Molkereiprodukte" in R. Liesegang's *Kolloidchemische Technologie* (Leipzig, 1929). The standard textbook of dairy chemistry for many years has been H. Droop Richmond's *Dairy Chemistry* (London, 1914).

# CHAPTER XIV

# SMOKE DAMAGE AND PLANT PROTECTION

It might appear evident at first sight that few living objects are less likely to be brought under the influence of external colloidal systems than the aerial parts of plants. Under ideal conditions this is undoubtedly the case. They project upwards into a mixture of four gases, three of which, oxygen, carbon dioxide and water vapour, are intimately concerned as molecules in their life processes. Conditions, however, are not always ideal. In the neighbourhood of great centres of industry the atmosphere contains abundant colloidal particles in the form of soot or dust which eventually settle on the foliage, where their influence is almost wholly harmful. Yet, on the other hand, the careful grower seeks to diminish the ravages of insect pests and plant diseases by the application of insecticides and fungicides, most of which have justifiable claims to be considered as colloidal systems. They are now so numerous that it would be quite impracticable to discuss them singly and we can only indicate in this chapter the broad outlines of the theory which lies behind their development.

**Smoke Damage.**—The subject of solid-gaseous or liquid-gaseous colloidal systems in which a solid or liquid is dispersed as fine particles in a gas has only, so far, been mentioned in passing. These systems have somewhat peculiar properties, which we must briefly consider before discussing the harmful effects of smoke and dust on vegetation. Two points immediately stand out when disperse systems in liquids and in gases are compared. Firstly, gaseous dispersions contain fewer and larger particles than most other colloidal systems. Secondly, they are inherently unstable. This instability is due to the fact that in gases, which are almost perfect insulators, dissociation into ions is impossible so that the electrical double layer around the particle no longer exists. With it is removed one of the greatest stabilizing factors. Colloidal particles dispersed in a gas often carry small electric charges which are unbalanced by any ions in the gas, but these may be both positive and negative in the same system. When particles collide, therefore, there is little to keep them apart, and coagulation proceeds continually.

The number of smoke particles in town air varies enormously, 200,000 per c.c. have been recorded in dense fog, and 1000 per c.c. in clear weather in towns. The coagulation of smokes obeys essentially the same laws as that of collodial particles in liquids. Just as in liquid systems coagulation becomes too slow to be measurable when less than $10^7$ particles per c.c. are present, so also in gases there is a similar lower limit of about $2 \times 10^4$ particles per c.c. This is one of the reasons why fogs may persist for some days, in spite of the unceasing coagulation. Another reason is that the rate of fall of small smoke particles in air is not sufficient to clear the atmosphere rapidly. It has been shown that particles $2\,\mu$ in diameter settle at the rate of about 0·1 mm. per second, and many of the smoke particles are smaller than this.

The composition of smoke particles varies with their origin and with the atmospheric conditions prevailing.

Carbon is usually the chief constituent, but mineral matter and tar are also present, along with smaller quantities of ammonium salts and sulphuric acid. Industrial soot has a much lower content of carbon and volatile matter than domestic soot obtained by the burning of coal in open grates. (The use of soot as a fertilizer depends chiefly on its content of nitrogen in the form of ammonium salts, which varies from nil in many industrial soots to 5 per cent. in domestic samples.) As soon as the atmosphere becomes saturated with moisture and a fall in temperature is experienced the water vapour condenses on the smoke particles. This increases their size and causes them to fall more rapidly, but often not quickly enough to clear the atmosphere. A fog results which may persist even when the conditions have become drier. The tarry matter in the soot forms a film around the water droplets, so hindering free evaporation.

The effect on plants is partly physical and partly chemical. The soot particles which adhere strongly to foliage by virtue of their tar content, block up many of the stomata of the leaves. The assimilation of carbon dioxide is thereby reduced and the rate of growth falls accordingly. This is very marked in the case of evergreens. The chemical effect is caused by the free sulphuric acid present which gives to the leaves a blotched and even perforated appearance, leading to premature withering and defoliation. It also acts indirectly in denuding the soil of its exchangeable bases, which results in time in the high lime requirements found for many soils in industrial areas.

**Plant Protection.**—The toxic substances which the farmer and horticulturist use in the protection of their crops are usually divided into two classes, insecticides and fungicides ; then these are subdivided according to their mode of action on the organisms concerned. In any case the main principles involved in the actual application are the same. The first requirement is that every part of the plant above ground shall receive sufficient of the toxic substance. Now ideally this condition would be most readily met by the use of a gas or vapour, whose molecules are, of course, free to diffuse to every surface which the plant presents to the atmosphere. This is fumigation, largely practised in indoor culture but also applicable in the open where the crop can be temporarily covered. It suffers from the disadvantage that only a few suitable toxic substances are sufficiently volatile. The non-volatile ones cannot be applied in any form which even approaches the molecular state of dispersion. We have seen in dealing with smoke and dust that it is impossible to have a high concentration of small colloidal particles suspended in a gas, owing to the ceaseless coagulation. There exists, therefore, an enormous gap between the largest molecule which is sufficiently volatile to be serviceable and the smallest particles of solid or liquid which are stable enough to remain suspended in the atmosphere for the necessary time. Roughly speaking, the range from 1 $m\mu$ to 100 $m\mu$ is closed, but as we shall see shortly, part of it can be approached indirectly.

We have now to consider how this problem of " covering power " can be solved, starting from compact material and proceeding to greater and greater degrees of dispersion. Consider 1 sq. cm. of leaf surface. A single compact cubical particle covering this would have a volume of 1 c.c. If, however, the cube were subdivided into 1000 small cubes, each 0·1 cm. in length, then 100 of these would cover the square centimetre and only 0·1 c.cm. of material would be required. Thus we see that the amount of material required to cover a given area with a single layer of particles is proportional to their linear dimensions. With particles of 1 $\mu$, only 0·0001 c.cm. of material would be needed to cover each square centimetre of surface. For economy and efficiency, therefore, it is desirable to apply the toxic substances at the highest possible degree of dispersion. This aspect of the matter has long been appreciated both by users and manufacturers, and the word colloidal is now appearing very frequently in advertisements, sometimes, one regrets to find, with little justification. As regards solids such as sulphur which are applied by blowing the finely divided material over the plants, it is extremely doubtful whether any great advantage can yet be secured by using material whose particles are less than 1–2 $\mu$. The reason is that the dispersion process, even with particles of this size, is so inefficient that they float into the air chiefly as aggregates and settle as such on the plant. The dispersion of pure liquids by sprays and "atomizers" does not, as a rule, lead to particles smaller than 5 $\mu$, and since considerable power would be required to break up the droplets further, the indirect method of application is probably cheaper and more efficient.

This indirect method which can be used both for solids and liquids will now be discussed. The toxic substance is here used as a suspension or an emulsion in water and this disperse system is applied to the plants by spraying. The water then evaporates, leaving the toxic substance spread in a thin layer over the foliage. In order to obtain a continuous film, which is particularly important for fungicides, three conditions are necessary. The suspended particles must be small and must remain so as the liquid evaporates ; they must be present in sufficient concentration ; and the foliage must be completely wetted by the liquid. Now it is fortunate that these conditions are all compatible with one another and that the addition of a single substance, if carefully chosen, will allow of all three being fulfilled. The choice obviously lies amongst those hydrophile colloids which have a strong protective action, such as gelatin, albumin, starch, gums, the saponins, the lecithins and soaps. It is an advantage to add such a substance during the preparation of the colloidal system for it then greatly assists in the production of very small particles. These it subsequently protects from coagulation both in storage and during the evaporation of the water from the plant. If added in sufficient amount it also functions as a "spreader," that is, it causes the liquid to wet the surface completely instead of remaining as separated drops. The mechanism of this process will be clear from what has already been said in Chapter IV, about the action of strongly adsorbed molecules at interfaces. The colloids used as spreaders are those which are also strongly adsorbed and which therefore greatly reduce the interfacial tension at the leaf-water boundary.

Yet a fourth duty may be required of this colloidal "maid of all work." Where spraying is done as a preventative measure it is important that the film of toxic substance should adhere for some time, and the obvious method of securing this is by choosing a single colloid which will act as protective agent, spreader and adhesive. This narrows the field of choice somewhat, but the manufacturer has still a considerable selection available. A more subtle way of securing adhesion is by making the toxic colloidal particles carry the opposite sign of charge from the leaf surface.

A simple example of these principles is afforded by the use of casein preparations or even of separated milk in the making of Bordeaux mixture. The casein is, as we already know, highly dispersed in alkaline solution and acts as a protective agent, spreader and adhesive. Its action in this last category is not so important as its effect as a spreader, since freshly made Bordeaux mixture adheres well without addition of colloids.

The emulsification of oils by addition of soaps has already been discussed ; one can only add here that a very high degree of dispersion need not always be attained, since it has been shown that paraffin emulsions are more effective against aphids when the droplets of the oil are large.

On the whole, however, there are comparatively few of the insecticides and fungicides which the farmer and horticulturist can make for himself. He is largely in the hands of the manufacturer and his judgment can only be based on his own experience and on the advice of others. To this the chemist can add but little. His analyses may enable him to reject the utterly worthless materials, but they would seldom enable him to assign a definite order of effectiveness to the more reliable products. Amongst the arsenical insecticides, for instance, an assessment on the basis of arsenic content might be completely misleading. Particle size, which is a measure of covering power, and the choice of protective colloid, spreader or adhesive are also of fundamental importance. The investigation of each of these points in detail would comprise a piece of research in itself. As yet there have been so few of these investigations that the chemist has little to guide him when he is asked to give an opinion on some new-comer to the long list of proprietory toxic agents.

## SUPPLEMENTARY READING

In J. B. Cohen and A. G. Ruston's *Smoke, A Study of Town Air* (2nd ed., London, 1925) the effect of smoke on vegetation is considered in detail, with many excellent illustrations. A development of the scientific principles and the practical methods for the study of smokes as colloidal systems is found in R. Whytlaw-Gray and H. S. Patterson's *Smoke, A Study of Aerial Disperse Systems* (London, 1932).

A detailed and critical account is given of the whole range of insecticides and fungicides in H. Martin's *The Scientific Principles of Plant Protection* (London, 1928). In Liesegang's *Kolloidchemische Technologie* (Leipzig, 1929), the chapter by A. Chwala on "Der Pflanzenschutz" stresses the importance of the colloidal character from the point of view both of the user and the manufacturer of insecticides and fungicides.

# INDEX

Absorption, 37
Acetic Acid, dissociation of, 47
Acid, weak, insoluble, dissociation of, 45
Adhesives, 176
Adsorption, 37, laws of, 39 ; of water vapour, 127
Ageing, 13
Albite, 112
Albumin, egg, 143, 145
Albuminoids, 148
Albumins, 147, 148, 176
Alcohols, 33
Alkali soils, 116, reclamation of, 117
Alkaloids, 34
Alum, 9
Aluminium hydroxide, 54, 74, 112
Amines, 34
Amino-acids, 141
Ammonia, sulphate of, in soils, 86
Ammonium salts in smokes, 173
Amorphous, 13, 38
Amphoteric, 142 ; surface, 115
Anhydromaltose, 139
Anion, colloidal, 46 ; exchange, 56
Apatite, 75
Atomizer, 175

Base exchange, 55, 79, laws of, 80
Bases, coagulation by, 91 ; exchangeable, 78, 109
Beidellite, 79, 81, 88, 113
Bemmelen, J. van, 101
Berzelius, 101
Black alkali, 117 ; earths, 118, 132
Bordeaux mixture, 177
Boulder clays, 114
Bound water, 67
Brown, R., 17
Brownian movement, 17, in dissociation, 46
Butter, 167, water globules in, 169
Butter-fat emulsion, 160 ; globules, rise of, 25, sizes of, 161

Calcite, 85
Calcium, caseinate, 164 ; chloride as coagulator, 90 ; clay, 92, cataphoresis and coagulation of, 89, 90 ; humate, 107 ; hydroxide as coagulator, 93
Capillarity, 34
Capillary water, 127
Capillary-active, 34, molecules, structure of, 36
Carbohydrates, 136
Carbon in smoke, 173
Cardioid ultramicroscope, 30
Casein, 164, 170, 177, isoelectric point of, 165, molecular weight of, 165

Caseinogen, 148, 164
Caseose, 170
Catalysis at surfaces, 40
Cataphoresis, 48, 49, 89
Cataphoretic velocity, 89, 93
Cation, colloidal, 47, exchange, 55, 109
Cations, exchangeable, in clay lattice, 78
Cells, permeability of, 135; rigidity of, 135
Cellulose, 136, 140, 151, 152, composition of, 104
Chalk, 126
Charcoal, adsorption by, 38
Cheese, 170
Chestnut-coloured earths, 118
Chlorites, 76
Chromoproteins, 109
Churning, 168
Clay fraction, 71, 125, mineralogical character of, 79; gels, 94; minerals, 75; paste, 95; suspensions, elasticity of, 95
Clays, 54, 72; boulder, 114; colloidal properties of, 88; hydrogen, instability of, 120; shrinkage of, 97; thixotropy of, 95; vapour pressure of, 97
Coagulation, 13; by bases, 91; by frost, 131; effect of shape on, 24; effect of size on, 23; kinetics of, 22; of colloidal gold, 52; orthokinetic, 24; quick, 90; rapid, 22, 51; slow, 22, 51, 89, 96; theory of, 49
Coal, 102
Coarse sand fraction, 70, 125
Collageen, 143, 148, 159
Collisions, molecular, 11
Colloid chemistry, definition of, 2; mill, 14
Colloidal anion, 46; cation, 47; gold, 28, coagulation of, 52; systems, definition of, 7, optical properties of, 27, stability of, 50.
Colloids hydrophile, 52, 54, 59; hydrophobe, 52; irreversible, 53; mutual coagulation of, 57; reversible, 53
Colostrum, 167
Combining capacity of proteins, 144
Condensation methods, 13
Continuous phase, 6
Copper oxide, colloidal, 53; sulphate, vapour pressure of, 63
Covering power, 174
Cream, homogenized, 15; layer, formation of, 162
Critical concentration, 52; velocity, 89
Crumb formation, 132; structure of soil, 123
Crystallization, rate of, 12
Cultivation of soil, 123
Curvature of surface, effect on solubility, 9

Dialysis, 19
Diameter, equivalent, 71
Diffusion, 19
Disperse phase, 5
Dispersion, degree of, 5; medium, 6; methods, 14
Dissociation, 41, 42; at an interface, 45; Brownian movement in, 46; of a weak, insoluble acid, 45
Döbereiner's lamp, 40
Dolomite, 85
Double layer potential, 89
Drought resistance of plants, 68
Dynamometer, 125, 133

Edestin, 148
Egg albumin, 143, 145
Elastic gels, 60, 65 ; properties of gels, 62
Elasticity of clay suspensions, 95
Electrical double layer, 46
Electroendosmosis, 133
Electron, 43 ; valency, 43
Emulsification, 15
Emulsion, butter-fat, 160 ; paraffin, 33, 34, 177
Emulsions, breaking of, 35 ; inversion of, 35, 168
Emulsoid coating, 95
Equivalent diameter, 71
Erosion of soils, 132
Exchange reactions, ionic, 55, 80
Exchangeable bases, 78, 109

Fatty acids, 34
Felspars, 85, 114, decomposition of, 111 ; in silt, 79
Ferric hydroxide, 112, colloidal, 61, 73
Fertilizers, action of, 82, and soil texture, 131
Fibre structure, 151
Fibrin, coagulation of, 24
Fibrinogen, 148
Fibroin, 143, 151, 155
Film, monomolecular, 37
Fine sand fraction, 70
Flocculation, 22, of silt, 93
Foam, solid, 39
Freezing-point depression of milk, 167
Frost, coagulation by, 131, dehydration by, 131, effect of, 130
Fulvic acid fraction, 102, 106
Fumigation, 174
Fungicides, 14, 171, 174

Gel, definition of, 17, structure, 150
Gelatin, 60, 108, 143, 145, 176 ; protective action of, 62 ; vapour pressure curve of, 65
Gels, 59, clay, 94, elastic, 60, 62, 63, 97, hydration of, 136, non-elastic, 65, 97, water in, 63
Gibbsite, 74, 76
Gliadin, 148
Globin, 148
Globulins, 148
Glucoproteins, 148
Glutelius, 148
Glutenin, 148
Glycogen, 139
Gold, colloidal, 28, coagulation of, 52
Graphite, 39
Gums, 176
Gypsum, 116, 117, solubility of, 9

Hæmoglobin, 143, 145, 147
Hair, 157
Halloysite, 76
Helmholz, 42
Histone, 145, 148
Homogenizer, 14
Hordein, 148
Human milk, 167
Humic acid, composition of, 104 ; fraction, 102, 106 ; gel, 108 ; protective action of, 108, 120
Humic matter, 102, 115, 124, 126 ; colloidal properties of, 106 ; exchange capacity of, 105
Humin fraction, 102, 107
Humus, 83, 88, 101
Humus podsol, 120
Hydrated oxides, 72
Hydration of gels, 136, of ions, 54, 81

Hydrogen clay, 92, cataphoresis and coagulation of, 89; instability of, 120
Hydrogen ions, 45, adsorption of, 91
Hydrophile character of proteins, 145; colloids, 52, 54, 59
Hydrophobe colloids, 52
Hydroxy-acids, organic, 120
Hydroxyl ion, adsorption of, 56
Hymatomelanic acid fraction, 102, 106
Hysteresis, 61

Imbibitional moisture, 130
Insecticides, 14, 171, 173
Interface, 2
Interfacial tension, 34, effect of dissolved substances on, 34
Inulin, 139
Inversion of emulsions, 35, 168
Ionic exchange reactions, 55
Ionisation, 44
Iron podsol, 120
Isodyne, 126
Isoelectric point, 115, of proteins, 145

Kaolin group, 76, 98
Kaolinite, 76, 79, 112
Keratin, 148, 151, 157, 159
Kinetic energy of colloidal particles, 18; theory, 18

Lactalbumin, 147, 148, 166
Lactoglobulin, 166
Lactose, 160
Laterite, 112, 118
Lecithin in milk, 166
Lecithins, 176
Lecithoproteins, 147
Lichenin, 139
Liebig, J. von, 101
Lignin, 103, composition of, 104
Ligno-cellulose, 141
Lime, 126, physical effects of, 132
Lithium clay, cataphoresis and coagulation of, 89
Loss on ignition, 129

Magnesium clay, 93, cataphoresis and coagulation of, 89
Maximum capillary water capacity, 130
Mechanical analysis, 71, 124
Mechanical composition of soils, 70
Micas, 76
Micelle, 47
Micro-organisms, protoplasm of, 105
Milk, 160; homogenized, 162; human, 166; sugar, 160
Mineral colloids of soils, 69
Mineralogical character of clay fraction, 79; silt fraction, 79
Moisture content, 128; equivalent, 129; imbibitional, 130; relationships, 127
Molecular collisions, 11; weights of proteins, 143
Monomolecular film, 37
Montmorillonite, 79, 88, 114, group, 77
Mucin, 148
Mutual coagulation of colloids, 57
Myosin, 158

Newton, R., 66
Nitrate of soda in soils, 83
Nitrifying organisms, 86
Nitrogen in soils, 109
Non-elastic gels, 65, 97
Nontronite, 78
Nuclei, rate of formation of, 11, of growth of, 12
Nuclein, 148
Nucleohistone, 148

Nucleoproteins, 147
Nucleus, atomic, 43

Optical properties of colloidal systems, 27
Organic colloids of soils, 101; hydroxy-acids, 120
Orthoclase, 112
Orthokinetic coagulation, 24
Osmotic pressure, 20, laws of, 20; of starch sols, 138
Ovalbumin, 148
Ovoglobulin, 148

Paracasein, 170
Paraffin emulsion, 15, 33, 34, 177
Paste, clay, 95
Peat, 101; contraction and expansion of, 108
Peptization, 60, 94, 106, 108, 119
Peptizing agent, 61
Permutite, 93
Perrin, A., 42
Phase, continuous, 6, disperse, 5
Phosphates, 72, 74, insoluble, colloidal, 54
Phosphorus in soils, 109, in starch, 137
Plant protection, 171
Plasticity, 96
Plate-shaped particles, coagulation of, 24, fall in water, 26
Platinum black, 40; colloidal, 53
Podsol, 119; humus, 120; iron, 120
Polder, 117
Polydisperse systems, coagulation of, 94
Potassium chloride as coagulator, 90
Potassium clay, cataphoresis and coagulation of, 89, 90
Potential of double layer, 89
Profile, 119
Prolamins, 148
Protamines, 142, 145, 147, 148
Protective action, 62, 120, 163
Proteins, 141; combining capacity of, 144; composition of, 104; hydrophile character of, 147; isoelectric points of, 145; molecular weights of, 143; protective action of, 163; swelling of, 146
Protoplasm, 141; of micro-organisms, 105
Pseudo-viscosity, 96
Pyroxenes, 85

Quartz, 73, 93
Quincke, 42

Rennet, 170
Residual shrinkage, 98
Resistance of soil, 125
Reversible colloids, 40
Reversible reactions, 55
Rod-shaped particles, coagulation of, 24, fall in water, 26

Saline soils, 116
Salmin, 148
Saponins, 34, 176
Scleroproteins, 148
Seasonal variations in physical conditions, 130
Semi-permeable membrane, 20
Sensitization of fat globules by protein, 164
Serum albumin, 143, 145; globulin, 143, 145
Settling under gravity, 24
Silicic acid, 72, 93, 112; gel, 59, 98, 108; vapour pressure curves of, 65
Silt, flocculation of, 93; fraction, 71, 79, 125, mineralogical character of, 79
Silver, colloidal, 53

Single value soil constants, 126
Smoke damage, 171 ; particles, 172
Smokes, composition of, 173
Smoluchowski, 42
Soaps, 34, 168, 176, as protective agents, 15
Sodium caproate, 37 ; chloride, ionisation of, 43 ; clay, cataphoresis and coagulation of, 89, 90, 92 ; palmitate, 37 ; stearate, 36
Soil particles, rate of settling, 24
Solid foam, 39
Solonetz, 117
Solontschak, 117
Soot, 173
Sols, 59, definition of, 17
Solubility, influence of, 8
Solution, saturated, 9, supersaturated, 10
Sorption, 37
Spreaders, 176
Stability of colloidal systems, 50
Starch, 108, 136, 176 ; amylopectin fraction, 137 ; amylose fraction, 137 ; grains, 136 ; peptization of, 139 ; protective action of, 62 ; sols, osmotic pressure of, 138 ; swelling of, 137
Static rigidity, 96
Sticky point, 130
Stomata, 173
Sturin, 148
Subdivision, definition of, 6, degree of, 5
Sulphate of ammonia in soils, 86
Sulphur, 175
Supercooling of butter-fat, 164
Supersaturated solution, 10
Supersaturation, degree of, 10
Surface curvature, effect on solubility, 9
Surface ions, reactions of, 54
Suspensoid core, 93
Symmetry value, 81
Szik, 117

Talc, 76
Tar in smoke, 173
Tchernosem, 118
Texture of soils, 131
Thixotropy, 61, of clays, 95
Timothy, drought resistance of, 68
Tyndall cone, 27

Ultrafilter, collodion, 20
Ultrafiltration, 19
Ultramicroscope, cardioid, 30, slit, 29
Usar, 117

Valency electron, 43
Valonia ventricosa, 153
Vapour pressure curve of copper sulphate, 65, of gels, 65
Vapour pressure of clays, 97, of soils, 127
Viscosity, 61, effect of coagulation on, 61
Vitellin, 148

Water, bound, 67
Water in gels, 63
Western rye grass, drought resistance of, 68
Wheat, winter hardiness of, 66
White alkali soils, 116
Wiedemann, 42
Wilting coefficient, 129
Winter hardiness of plants, 66
Wool, 157

Xylene equivalent, 130

Zsigmondy, R., 28

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